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Collective surface modes of Ag single crystals

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We calculate the electron-energy-loss spectra and the normal surface modes of the low-index faces of Ag single crystals. To this end we develop a model that accounts for the surface crystalline geometry and for both intraband and interband transitions. We obtain surface response functions that display a resonant structure due to face- and orientation-dependent modes, which lead to an anisotropy in the loss spectra for finite momentum transfers. Furthermore, they lead to a large anisotropy in the optical reflectance.

The surface plasmon (SP) at the abrupt interface of a semi-infinite local metal has a frequency $\omega_{sp}(0)$ that is independent of wave vector[1] $\mathbf{Q}$ in the nonretarded limit. Spatial dispersion, the change in the electronic structure, and the presence of a smooth transition region at the interface lead to a dispersion[2] of $\omega_{sp}(Q)$, which differs from $\omega_{sp}(0)$ by a term expected to be linear in Q for small wave vectors. The coefficient of the linear term is related to the spatial distribution of the fluctuating charge,[3-5] and therefore, its determination comprises a test for theoretical models of the surface. Calculations for a semi-infinite electron gas confined by a self-consistent potential barrier[6] predict a negative slope, which has recently been experimentally confirmed by angle-resolved high-resolution electronic energy-loss spectroscopy (HREELS) of simple metals.[7] HREELS has also provided evidence[8] for the much debated multipolar surface mode.[9] However, the spectra for single-crystal surfaces of silver[10-12] display surprising results. A positive dispersion was found[10] for Ag(111) and[12] Ag(001). Afterwards, a quadratic dispersion was obtained[11] for both Ag(111) and Ag(110). Furthermore, a dependence of ω_{sp} on the surface orientation and, for (110), on the direction of $\mathbf{Q}$ was found, even in the $Q\rightarrow 0$ limit.[11] This limiting behavior was shown to be in error,[13,14] but the anisotropy of the SP dispersion for finite Q has been confirmed[14-16] although there is still disagreement on its kind (linear or parabolic). A face and direction dependence of the SP of silver was previously observed in the retarded region by attenuated total reflection measurements,[17] and other optical anisotropies have also been reported.[18,19]

The plasma frequencies of Ag are substantially lower than the free-electron-gas results due to the onset of interband transitions between a narrow d-band complex below the Fermi energy and the s-p conduction bands.[20] The bulk and surface plasma conditions $\epsilon=0$ and -1 are satisfied at frequencies close to the interband transition, where ϵ is the macroscopic dielectric response. Therefore, a theory that addresses the SP dispersion on Ag surfaces should incorporate both intraband and interband transitions as well as the crystalline geometry of the surface. The development of such a theory is the purpose of the present paper. We obtain important anisotropies even when the surface-induced change of the electronic structure is neglected.[19,21] Their origin is the screened surface-local-field[22] effect on resonant atomiclike polarization processes.

First, we recall that the d electrons are mostly localized around the ionic core positions. In the presence of an oscillating electric field, they contribute to the polarization only in those regions of space where their wave functions overlap those of the s-p bands. Then, around each ion we draw imaginary spheres large enough so that the interstitial region outside them contains predominantly conduction electrons with an approximately constant density. Each sphere contains both d electrons and conduction electrons but with a nonuniform distribution, besides an ionic core. If the spheres are nonoverlapping, the field induced in their exterior by their complicated contents can be expanded multipolarly. Therefore, we model the Ag crystal as a uniform electron gas out of which spherical cavities centered on the fcc lattice sites are carved. The cavities are occupied by polarizable entities characterized by a polarizability which accounts for interband transitions, the conduction currents within the spheres, the core polarization, and all intracavity interactions, i.e., we replace the core, the d, and the conduction electrons within each sphere by a suitable dipole at its center. The dynamic dipoles induced within different cavities are sources of an electric field which is screened by the electron gas on their outside. The qualitative ideas discussed above are consistent with the microscopic real-space calculations of the structure and response of noble-metal surfaces.[23,24] Similar ideas have been employed in calculations of the van der Waals molecule-surface interaction and in the absorption and photoemission yield of non-free-electron-like surfaces.[4,25]

We proceed by further assuming that our electronic gas has a local Drude response $\epsilon_g=1-\omega_p^2/(\omega^2+i\omega/\tau)$. Therefore, our calculation is complementary to the more

common jellium calculations, which take into account the spatial dispersion of the electron gas but neglect the crystalline structure.[3,4] A full calculation, unavailable at the present time, should incorporate both. The equation for the induced apparent dipoles is

$$\mathbf{p}'_i=\alpha'\left[\mathbf{E}_0+\sum_{j\neq i}T_{ij}\mathbf{p}'_j+\sum_{j'}T_{ij'}\mathbf{p}'_{j'}\right], \tag{1}$$

where $\mathbf{E}_0=(E^x,E^y,D^z/\epsilon_g)$ plays the role of an external long-wavelength field screened at the surface $z=0$ of the semi-infinite electron gas. The dipoles $\mathbf{p}'_j$ include the charges within the cavity centered at $\mathbf{R}_j$ together with the screening charges induced at its surface, while the image dipoles $\mathbf{p}'_{j'}=(\epsilon_g-1)/(\epsilon_g+1)S\mathbf{p}'_j$ with positions $\mathbf{R}_{j'}=S\mathbf{R}_j$ account for the charges induced at the boundary of the electron gas. Here, $T_{ab}=\nabla_a\nabla_a 1/R_{ab}$ is the unscreened dipole-dipole interaction tensor and $S=\mathrm{diag}(1,1,-1)$. Equation (1) defines the apparent polarizability $\alpha'(\omega)$ as the response of each cavity to the local field, i.e., the microscopic field excluding the self-field due to the charges within and the screening charges at the surface of the sphere. In the bulk, α' is related[26] to ϵ through the Clausius-Mossotti[27] relation $(\epsilon-\epsilon_g)/(\epsilon+2\epsilon_g)=4\pi n\alpha'/3$, where n is the number density of ions.

After a planewise sum of the dipole-dipole and the image-dipole interactions,[28] and assuming α' is independent of position, we solve Eq. (1) numerically[29] for $\mathbf{p}'_i$, and calculate[26] the surface conductivities[30]

$$\sigma=-i\omega a\frac{\epsilon-\epsilon_g}{4\pi}\sum_n\frac{(p'_n)_\parallel-(p'_B)_\parallel}{(p'_B)_\parallel},$$
$$s=-i\omega a\frac{\epsilon-\epsilon_g}{4\pi\epsilon\epsilon_g}\sum_n\frac{(p'_n)_\perp-(p'_B)_\perp}{(p'_B)_\perp}, \tag{2}$$

where B denotes bulk, a is the interplanar distance, and the sum over n is over crystalline planes. The surface conductivities are defined through $\mathbf{i}_\parallel=\sigma\mathbf{E}_\parallel(0)$ and $i_\perp=sD_\perp(0)$, where $\parallel$ and $\perp$ denote the directions parallel and perpendicular to the surface, $\mathbf{i}=\int d^3r(\mathbf{j}-\mathbf{j}_B)/A$ is the surface current, $\mathbf{j}$ and $\mathbf{j}_B$ are the current densities in our model and in a homogeneous semi-infinite system with response ϵ, and A is the area of the crystal's surface. The conductivities σ and s characterize the response of the surface to long-wavelength fields,[30] and are closely related to the parameters $d_\parallel$ and $d_\perp$ that are frequently employed in jellium calculations.[3,4]

The surface contribution to the EELS intensity can be written in the dipole scattering regime as[31,32] $I=J\,\mathrm{Im}r_p(\mathbf{Q},\omega)$, where J is a kinematical factor that depends on $\mathbf{Q}$, ω, the incident energy and the angle, and the properties of the crystal enter through its reflection amplitude r_p for p polarized fields. This is a useful approximation, although it ignores multiple scattering,[33] the change in direction upon dispersion, and the quantum interference between scattering before and after reflection by the surface,[31,34] whose experimental observation has recently been reported.[12] Nevertheless, it displays the close relation between the inelastic intensity and the reflection amplitude. For small Q, the latter may be obtained from the nonretarded limit of Eqs. (31) and (37) of Ref. 30,

$$r_p(\mathbf{Q},\omega)=\frac{\omega(\epsilon-1)+4\pi iQ(\sigma+\epsilon s)}{\omega(\epsilon+1)+4\pi iQ(\sigma-\epsilon s)}. \tag{3}$$

The surface electromagnetic modes of the system, given by the poles of r_p, may be observed as peaks in the inelastic intensity.

Using optically measured values[35] for ϵ we have calculated[26] the surface conductivities σ and s. Near the interband transition threshold they display resonances whose position, width, and strength depend on the crystal face and, in the case of σ, on the orientation of the electric field. These resonances correspond to self-sustained dipolar oscillations localized close to the surface. Their frequencies are shifted from the peak of the apparent polarizability α' due to the coupling among dipoles through the direct and image Coulomb fields. Their face and orientation dependence originates from the corresponding dependence of the dipolar sums.[28]

Figure 1 illustrates the reflection amplitude r_p as a function of frequency ω for a fixed value of Q ($=0.15$ Å^{-1}). Notice that the results for the (111) and the (100) surfaces display one peak each, slightly redshifted from the classical result $\hbar\omega_{sp}(0)\approx 3.63$ eV, for which[35] $\epsilon=-1$. This redshift originates from a small resonance in the normal surface conductivity s located near 3.75 eV. On the other hand, r_p shows a richer structure for the (110) face. Besides a much broader peak near $\omega_{sp}(0)$ and a new structure around 3.55 eV, there are two clearly noticeable peaks: one near 3.80 eV when $\mathbf{E}_\parallel\|$ [001] and one near 3.95 eV for $\mathbf{E}_\parallel\|[1\bar{1}0]$. These peaks arise from strong resonances[26] in the parallel conductivity σ centered at 3.70 and 3.85 eV for the [001] and [1$\bar{1}$0] directions, respectively.

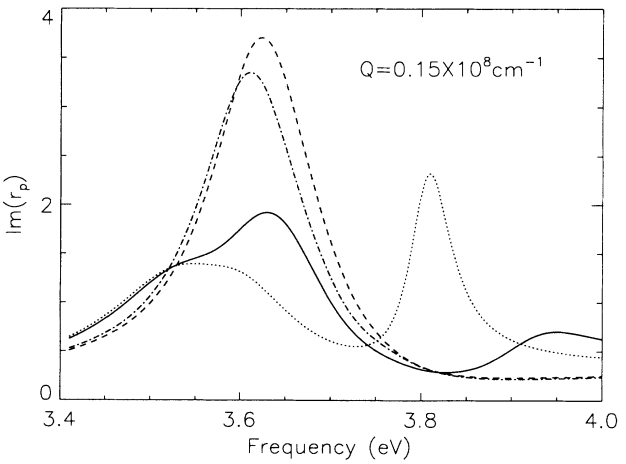

FIG. 1. Imaginary part of the reflection amplitude r_p for a p polarized field incident on a silver crystal, calculated for a fixed wave vector $Q=0.15$ Å^{-1} as a function of frequency ω. The solid curve corresponds to the (110) face when the parallel component of the field $\mathbf{E}_\parallel$ is along the [1$\bar{1}$0] direction. The dotted curve corresponds also to the (110) face but with $\mathbf{E}_\parallel\|$[001]. The dashed and dashed-dotted curves correspond to the (111) and (100) surfaces, respectively.

Figure 2 shows the dispersion relations for the collective modes of the low-index faces of an Ag crystal, obtained, emulating experiment, as the maxima of Im $[r_p(\mathbf{Q},\omega)]$ for each $\mathbf{Q}$. In the $Q\rightarrow 0$ limit there is only one mode at $\omega_{sp}(0)$. As Q increases the SP is redshifted and damped[26] by different amounts, depending on the face and propagation direction. For small $Q\approx 0.01$ and 0.03 Å^{-1}, new modes propagating along the $[1\bar{1}0]$ and [001] directions of the (110) face appear at energies 0.2 and 0.1 eV above $\hbar\omega_{sp}(0)$, respectively. Both of these new modes display a positive dispersion.

As Q increases, the coupling to the surface gets stronger since the field penetration diminishes, leading to the dispersion of the collective surface modes, as can be seen from the poles of Eq. (3), given approximately by

$$(\epsilon'+1)=4\pi Q(\sigma-\epsilon s)''/\omega \ . \tag{4}$$

For jellium, $\sigma=0$ and ϵ and s are structureless and approximately linear in ω near ω_{sp} so that a linear dispersion arises. The proximity of the surface-conductivity resonances to ω_{sp} leads to a richer behavior in Ag; the left-hand side (LHS) and the RHS of Eq. (4) might intersect one or more times depending on the line shape of the RHS and the magnitude of Q, and the dispersion might be positive or negative corresponding to a negative or positive slope of the RHS at the intersection point(s). In particular, different behaviors would result whether the resonances of the RHS precede or follow[26] $\omega_{sp}(0)$. The strength and position of our calculated resonances are sensitive to ω_g and to the distance from the first crystalline plane to the electron gas edge z_0, which are a measure of the screening by the electron gas in the interstitial region and near the surface.[26] We chose $\hbar\omega_g=7.5$ eV, $z_0=a/2$, and also $\tau=400/\omega_g$. However, we remark that the dipole-dipole interaction has large wave-vector components and therefore we expect our local model to exaggerate its screening.

Employing the same σ's and Eq. (40) of Ref. 30, we also calculated the surface corrections to Fresnel's expression for the normal-incidence optical reflectance of

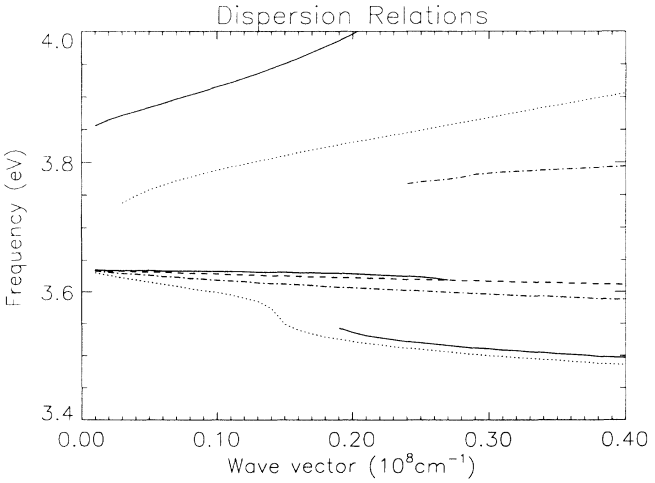

FIG. 2. Dispersion relations ω vs Q of the normal modes propagating along the $[1\bar{1}0]$ (solid) and [001] (dotted) directions of Ag (110), and on the (111) (dashed) and (100) (dash-dotted) surfaces.

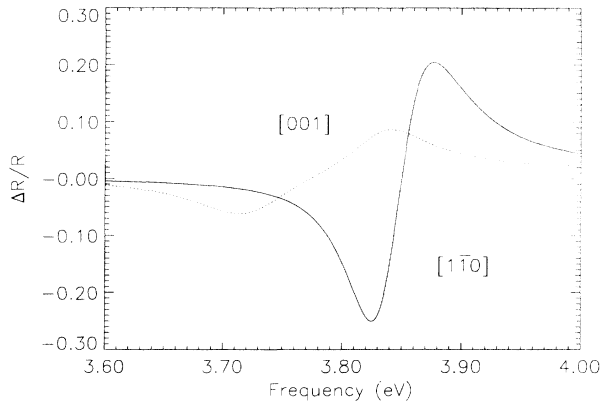

FIG. 3. Normal incidence differential optical reflectance $\Delta R/R$ vs ω of a (110) Ag surface $\mathbf{E}_{\parallel}\|[1\bar{1}0]$ (solid) and [001] (dotted).

(110) Ag. The differential reflectance shown in Fig. 3 is very large and depends on the orientation of the polarization vector. Therefore, it can be detected as a surface-induced optical anisotropy. Previous calculations have produced anisotropies[22] for semiconductor surfaces which, although two orders of magnitude smaller, have been observed.[36] Their measurement has proved very useful as a surface probe, even within hostile environments.[37]

In summary, we calculated the surface conductivity, EELS spectra, surface mode dispersion, and optical reflectivity of the low-index faces of single Ag crystals, introducing a model that incorporates both interband and intraband transitions, the surface geometry, and the surface local-field effect, within a long-wavelength approximation. For the (110) face we obtained new modes propagating along [001] and $[1\bar{1}0]$ with a small, although finite, lower Q cutoff. Their origin is the resonant structure of the surface response to $\mathbf{E}_{\parallel}$, unlike jellium where it is null. For the (111) and (100) faces we obtained a SP with a small negative dispersion.

Although our results disagree with the measured EELS spectra[10,12,16] they reveal the importance of the screened surface local-field effect at noble-metal surfaces and of the structure of the frequently neglected parallel conductivity σ. Furthermore, we have predicted a very large optical anisotropy, which has very recently been observed experimentally.[38] Further theoretical developments[39] for the calculation of the surface screening in real crystals are required in order to incorporate the spatial dispersion, the surface density profile, and the contribution to the surface response of the electron as, as well as the surface modifications to the bulk interband transitions and transitions involving surface states.

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