Multipole surface-plasmon-excitation enhancement in metals

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We consider the energy losses undergone by an electron reflected inside the extended electron-density distribution at the surface of a metal. The random-phase approximation calculation of the dynamical response with a local-density approximation ground state reveals the dramatic enhancement of the multipole-plasmon intensity compared with the conventionally considered reflection in vacuum above the surface. Our calculations conciliate the theory and the electron-energy-loss spectroscopy experiment with regard to the multipole surface-plasmon intensity, which has been predicted by previous theories to be two orders of magnitude smaller than the experimental one. The influence of the nonzero electron density along the incident electron path on the surface and the bulk-plasmon generation is also discussed. [S0163-1829(99)00115-0]

Multipole-plasmon (MP) modes at metal surfaces were predicted by Bennett within the hydrodynamic approximation.[1] In recent years, the excitation of these modes was demonstrated experimentally by the use of electron-energy-loss spectroscopy[2,3] (EELS) and supported theoretically by quantum-mechanical calculations.[2] A good agreement between theory and experiment had been achieved in these works for simple metals with regard to the monopole and multipole surface-plasmon dispersion and damping.

However, for all the metals dealt with and for all the geometries of electron scattering assumed the calculated spectra demonstrated a very weak MP peak, compared with the monopole surface-plasmon (SP) one,[2] while experimentally (e.g., in the case of K and Na) SP and MP peaks display themselves on an equal footing.[2,3]

Let us recall that the surface energy-loss function, introduced in Ref. 4 and conventionally used to describe the inelastic scattering at surfaces, by its definition pertains to the reflection in vacuum above the surface (dipole regime). This means that for models with abrupt static electron-density fall off, reflection of a charge is assumed to occur outside the electron density of the target. For self-consistent extended static electron densities, such as that of Lang and Kohn (LK),[5] this suggests that reflection takes place at negligible charge density, mathematically at infinity above the surface. Meanwhile it is clear that the back scattering of the incident beam is due to the reflection from the lattice and LK electron density is not negligible at the turning point of incident charges (impact regime). It could be supposed then that the discrepancy between the theory and the experiment with regard to the MP intensities was due to utilizing the dipole-regime theory to account for the impact-regime experiment.

Recently the formalism accounting for ions penetrating the surface of a solid has been developed.[6] However, these works deal with the ion-stimulated electron emission and do not address the problem of MP excitation in EELS. The purpose of the present work is to follow SP, MP, and bulk-plasmon (BP) behavior depending on the penetration depth of probing charges. We use LK densities of unperturbed jellium surfaces of K, Na, and Al to calculate the random-phase approximation (RPA) response to an external charge reflected at diverse distances to both sides of the surface. For reflection at the jellium edge we find the intensity of MP to be much larger than that obtained in Ref. 2 for reflection in vacuum. When the penetration increases under the edge, MP intensities for K and Na continue to grow, while for Al it merges with the left wing of BP, both conclusions being in agreement with experiment.

The inelastic scattering of a charge reflected at $z=c$ can be characterized by the energy-loss function[7]

$$L(\omega,q_\parallel)=-\frac{q_\parallel}{(2\pi)^2}\mathrm{Im}\int dq_z dk_z \frac{e^{i(q_z-k_z)c}}{(k_z^2+q_\parallel^2)}\epsilon^{-1}(q_z,k_z,q_\parallel,\omega)$$
$$\times\left[\frac{1}{p-p'+\mathbf{p}'\mathbf{q}/p'+i0_+}+\frac{1}{p'-p-\mathbf{p}\mathbf{q}/p+i0_+}\right]$$
$$\times\left[\frac{1}{p-p'+\mathbf{p}'\mathbf{k}/p'-i0_+}+\frac{1}{p'-p-\mathbf{p}\mathbf{k}/p-i0_+}\right], \tag{1}$$

where $\mathbf{p}$ and $\mathbf{p}'$ are the momentum of the charge before and after the scattering, $\mathbf{q}_\parallel=\mathbf{p}_\parallel-\mathbf{p}'_\parallel$ and $\omega=p^2-p'^2$ are the momentum and the energy loss, and the inverse dielectric function ϵ^{-1} is defined by the nonlocal relation

$$\phi(q_z,q_\parallel,\omega)=\int \epsilon^{-1}(q_z,k_z,q_\parallel,\omega)\phi_{\mathrm{ext}}(k_z,q_\parallel,\omega)dk_z,$$

where ϕ_{ext} and ϕ are the external and the total scalar potentials. Energy is measured in rydbergs. In real space, we have to solve the integral equation

$$\phi(z)-\int_{-\infty}^{\infty}\Pi(z,z')\phi(z')dz'=\phi_{\mathrm{ext}}(z), \tag{2}$$

where in RPA

$$\Pi(z,z',q_\parallel,\omega)=\frac{2\pi}{q_\parallel}\int_{-\infty}^{\infty}e^{-q_\parallel|z-z''|}\chi^0(z'',z',q_\parallel,\omega)dz'',$$

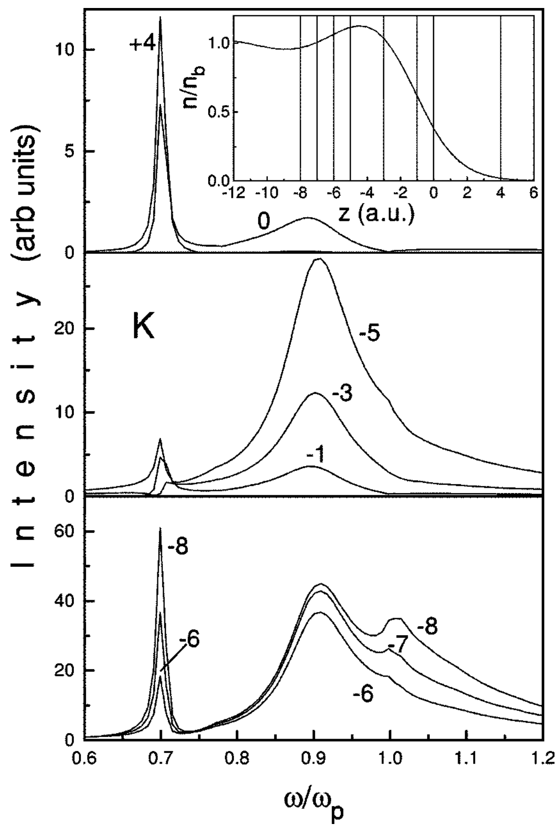

FIG. 1. Energy-loss function calculated for K surface ($r_s=5$) for reflection at different distances c from the jellium edge. The inset shows the penetration depths inside the charge-density distribution. $E_p=15$ eV, $\theta_i=50°$, and $\theta_f=60°$.

with the independent-particle susceptibility

$$\chi^0(z,z')=\frac{1}{\pi}\int d\mathbf{p}_\parallel dp_{z1}dp_{z2}\psi^*_{p1}(z)\psi_{p1}(z')\psi_{p2}(z)\psi^*_{p2}(z')\times\frac{f[(\mathbf{p_{1z}}+\mathbf{p}_\parallel)^2]-f[(\mathbf{p_{2z}}+\mathbf{p}_\parallel+\mathbf{q}_\parallel)^2]}{\omega+i0_++p^2_{1z}-p^2_{2z}+p^2_\parallel-(\mathbf{p}_\parallel+\mathbf{q}_\parallel)^2}. \quad (3)$$

$\psi_p(z)$ are the wave functions of the ground state jellium and f is the Fermi function, temperature assumed to be zero. $\phi_{\rm ext}$ is created by the charge density of the incident electron

$$\rho_{\rm ext}(z,q_\parallel)=\{\exp[iq_f(z-c)]/\cos\theta_f+\exp[iq_i(z-c)]/\cos\theta_i\}\Theta(z-c)/4\pi, \quad (4)$$

where $\Theta(z)=0,1$ if $z\leqslant,>0,q_{f,i}=\pm(p'-p-q_\parallel\sin\theta_{f,i})/\cos\theta_{f,i}$, and θ_i and θ_f are the angles of incidence and reflection. Then by Eq. (1)

$$L(\omega,q_\parallel)=-q_\parallel\ \mathrm{Im}\int_c^\infty\rho^*_{\rm ext}(z)\phi(z)dz.$$

Susceptibility (3) can be expressed by[8,2]

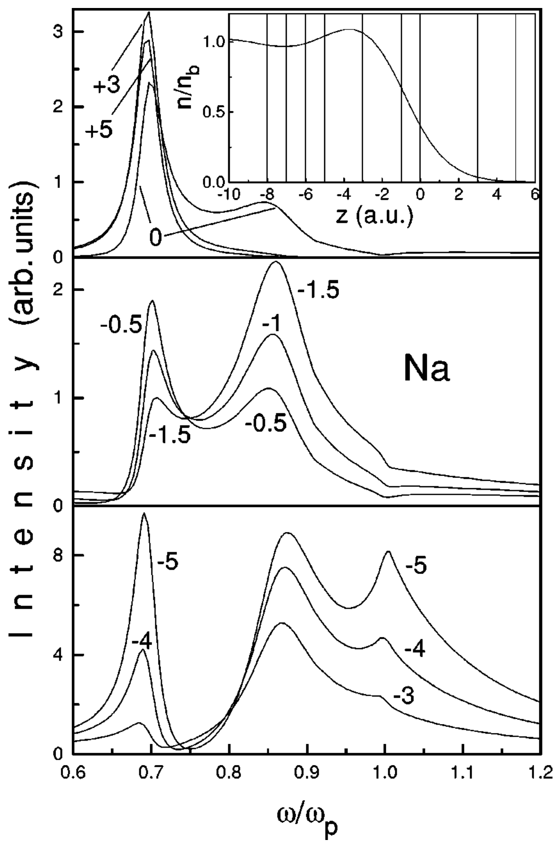

FIG. 2. The same as Fig. 1 but for Na ($r_s=4$) surface. $E_p=15$ eV, $\theta_i=44°$, and $\theta_f=60°$.

$$\chi^0(z,z')=\frac{1}{\pi}\int d\mathbf{p}_\parallel dp_z f[(\mathbf{p}_z+\mathbf{p}_\parallel)^2]\psi_p(z)\psi_p(z')\times[G(z,z',\omega+p_z^2-2\mathbf{p}_\parallel\mathbf{q}_\parallel-q_\parallel^2)+G^*(z,z',-\omega+p_z^2+2\mathbf{p}_\parallel\mathbf{q}_\parallel-q_\parallel^2)],$$

where the Green function is constructed as

$$G(z,z',\Omega)=[\psi^+_\Omega(z)\psi^-_\Omega(z')\Theta(z-z')+\psi^+_\Omega(z')\times\psi^-_\Omega(z)\Theta(z'-z)]/W(\Omega),$$

and the functions $\psi^\pm_\Omega(z)$ satisfy the Schrödinger equation

$$\left[\Omega+\frac{d^2}{dz^2}-V(z)\right]\psi^\pm_\Omega(z)=0,$$

with the asymptotic boundary conditions $\lim_{z\to\pm\infty}\psi^\pm_\Omega(z)=\exp(\pm\sqrt{\Omega}z).W(\Omega)$ is the Wronskian between $\psi^\pm_\Omega(z)$. This formulation includes all the final states above the vacuum level, unlike the direct use of Eq. (3) with the necessary integration cutoff.

We performed calculations by the above scheme with LK potentials of the jellium surface.[5] In Figs. 1, 2, and 3 the energy-loss functions obtained for reflection at different distances from the jellium edge of K, Na, and Al are presented. The corresponding reflection planes (shown in the insets) are chosen to show the strong penetration dependence of plasmon peaks. For K and Na, the intensity of MP grows monotonously with the penetration. The BP peak grows as well,

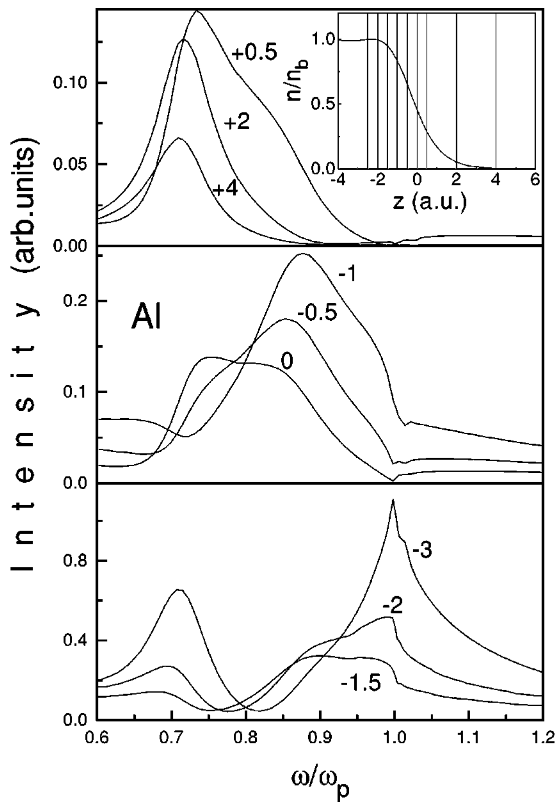

FIG. 3. The same as Fig. 1 but for Al ($r_s = 2$) surface. $E_p = 30$ eV, $\theta_i = 35°$, and $\theta_f = 60°$.

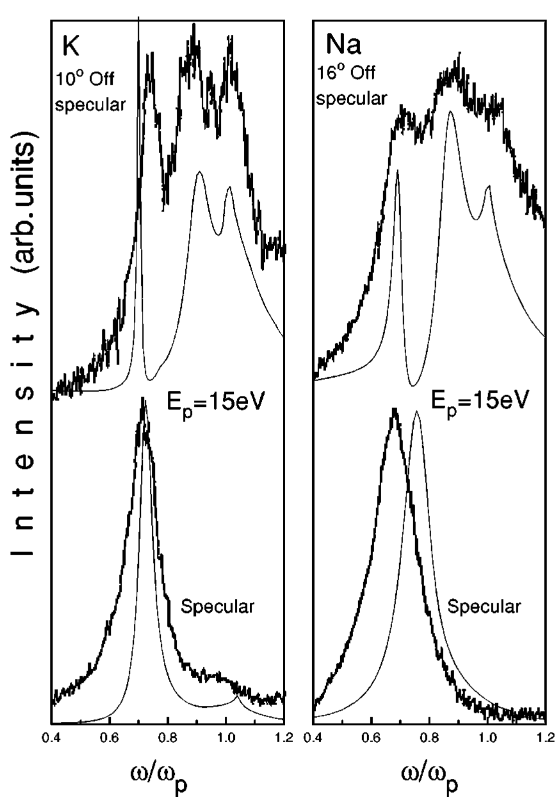

FIG. 4. Calculated energy-loss functions for K and Na surfaces and the experimental EEL spectra (noisy curves) from Ref. 2. $c = -8.5$ and -4.5 a.u. are taken for K and Na, respectively.

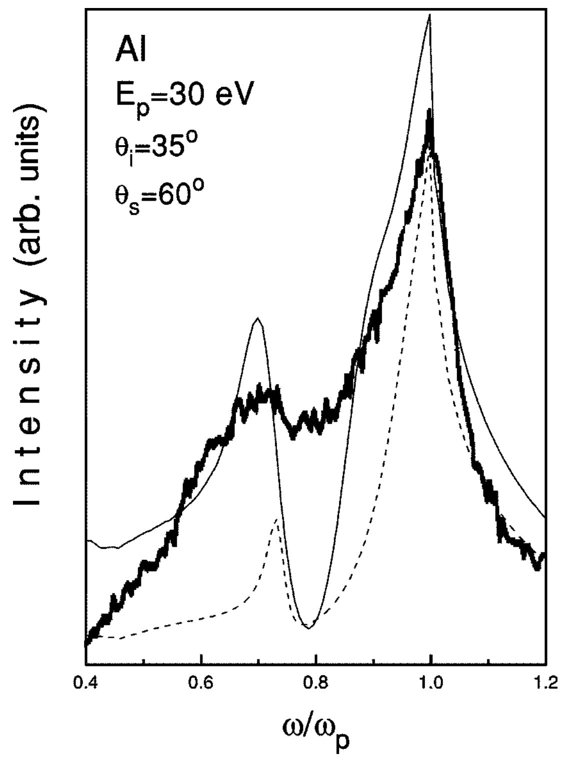

FIG. 5. Calculated energy-loss functions for Al surface and the experimental EEL spectrum (noisy curve) from Ref. 10. $c = -2.25$ a.u. is taken, which corresponds to the first atomic layer of the (111) face. The solid and the dashed curves are the jellium and the crystallinity included results, respectively.

starting from larger depths. In the case of Al, MP appears starting from $c \approx +0.5$ a.u., grows in amplitude, and shifts to higher energies influenced by the rising BP, until the former merges with the left wing of the latter.

In Figs. 4 and 5 the theoretical curves in a qualitative agreement with the experimental spectra for K, Na, and Al are presented. For K and Na, our calculation demonstrates the pronounced MP and BP peaks in the off-specular geometry.[9] The penetration should be about 8.5 and 4.5 a.u. for K and Na, respectively, to match the observed relative intensities of plasmons. For the (100) face these values lie between the second and the third atomic layers for K and between the first and the second ones for Na, the first layer assumed to be at half the interplane distance from the jellium edge. For Al, experiment does not reveal any trace of MP, which is the case with the theory starting from $c \approx -3$ a.u. This value lies between the first (-2.21 a.u.) and the second (-6.63 a.u.) layers in this direction, much closer to the first one.

Although our jellium calculations show reasonable agreement with experiment, let us discuss the possible extensions beyond this model. Unlike BP and SP energies, which in the long-wave limit are the bulk quantities of a medium, the energy of the MP mode depends crucially on the static charge density at the surface.[11] The general tendency is that the steeper is the density fall off the closer to unity is the ratio of MP and BP energies, until the two modes merge in the infinite barrier limit. It is also known that the electron density at the Al(111) surface becomes steeper than that of jellium if the crystalline potential is included.[12,13] We have calculated the spectrum of Al(111) with the crystalline potential from Ref. 12 (dashed line in Fig. 5). It can be seen that the crystallinity further decreases the penetration needed for MP to fade at the left wing of BP, making reflection from the first layer consistent with the experiment.

We are now in a position to explain the behavior of the SP, MP, and BP peaks in the EELS under reflection geometry. First we can assert that unlike the dipole mode calculations, for all the metals considered the account of the nonzero electron density along the incident electron path gives rise to the pronounced MP peak. The reason why MP is observed in EELS on alkali metals and it is not observed on Al is the difference in the steepness of the electron-density fall off at surfaces of these metals. For alkali metals, the position of the first and the second (for K, also the third) atomic planes is not deep enough in the bulk (for the corresponding electron densities), so all three peaks are well resolved in the off-specular geometry. On the contrary, for Al the reflection from the very first atomic plane results in a strong BP peak. MP in EELS would be seen on Al, as is the case with the photoyield measurements[14] when BP does not interfere with the spectrum, if the penetration could be less than the first atomic layer, but this is obviously impossible experimentally.

In all cases SP amplitude demonstrates nonmonotonous behavior with penetration. When c decreases from the positive values, SP first grows as $e^{-2q_{\|}c}$.[7] The subsequent fall in SP amplitude is related to the decrease of the external potential near the edge due to the incident and the reflected field interference, as can be verified explicitly from Eq. (4) and the fact that the strength of SP is roughly proportional to $\phi_{\mathrm{ext}}(z=0)$, as can be seen from the simple infinite barrier model. When c moves on into the bulk, SP rises again, as $\phi_{\mathrm{ext}}(z=0)$ increases.

In conclusion, the multipole-plasmon excitation in the impact-regime reflection EELS is explained in the framework of the impact-regime theory. The RPA calculation of the dynamical screening of an incident charge reflected inside the distributed charge density at a simple metal surface demonstrates high sensitivity of MP amplitude to the penetration depth of the probe. Our results account for the observed MP amplitudes for K and Na, which are about two orders of magnitude larger than those previously obtained in the dipole regime. For Al, our calculation also gives the considerable increase of MP intensity at very small penetrations, which then, in accord with experiment, disappears at experimentally achievable penetrations.

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