Angular Dependence of Dipole Scattering Cross Section: Surface-Plasmon Losses on Ag(100)

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We report high-resolution angular-resolved electron-energy-loss measurements of the cross section of surface-plasmon excitation. The intensity shows a pronounced minimum as a function of exchanged momentum near $q_{\parallel}=0$ whose position depends on impact energy and angle of incidence of the electron beam and is determined by the value of the phase shift occurring in the scattering process. The effect has been taken into account in the determination of energy and dispersion of the surface plasmon of Ag(100). A linear dispersion is found in the range of $q_{\parallel}$ between 0 and 0.15 Å^{-1} in contrast to the quadratic behavior found for Ag(111) and Ag(110).

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Because of its high surface sensitivity, high-resolution electron-energy-loss spectroscopy (HREELS) has emerged as a major tool for studying vibrational and electronic properties of clean and adsorbate covered surfaces.[1] This method has been applied for the first time to surface plasmons of clean metallic single-crystal surfaces by Contini and Layet[2] who investigated Ag(111). They measured plasmon dispersion and energy obtaining a quadratic behavior versus exchanged momentum $q_{\parallel}$ and a plasmon energy of 3.69 eV at $q_{\parallel}=0$. Recently, a more accurate HREELS study was performed by Suto *et al.*[3] on Ag(111) and Ag(110). The dependence of plasmon energy versus momentum was again quadratic and plasmon energy and dispersion were found to depend strongly both on crystal face and, in case of Ag(110), also on azimuth, indicating a complex nature of noble-metal surfaces and the necessity to widen the basis of available experimental knowledge.

In this Letter we present a study of the plasmon spectrum of Ag(100) by angle-resolved HREELS and the first investigation of the inelastic cross section for plasmon excitation. The data confirm the already established face[3] dependence of plasmon energy, but show in contrast an unambiguously linear dispersion of the loss frequency with exchanged momentum. The angular dependence of the inelastic cross section evidences the presence of a minimum clearly shifted away from $q_{\parallel}=0$ because of the interference which takes place between waves corresponding to reflection-before-loss and loss-before-reflection events so that its position determines the phase shift. Although scientists working with electron scattering have always been aware of the phase problem, this effect was so far never observed and constitutes a unique experimental method to determine both amplitude and phase associated with specular reflection.

For the experiment the Ag(100) single crystal has been prepared following conventional procedures. Sulfur and carbon were removed from the sample by cycles of neon-ion bombardment and annealing to an extent that even after annealing at 750 K and cooling to room temperature, their concentration was below the detection limit of the EELS. Care was taken not to heat the crystal beyond this temperature to avoid surface evaporation and reconstruction.[4] The plasmon losses were measured with the EELS used in earlier experiments.[5] The energy resolution of the primary electron beam was lowered to 20 meV in order to improve the signal-to-noise ratio for off-specular measurements. The limiting factor in

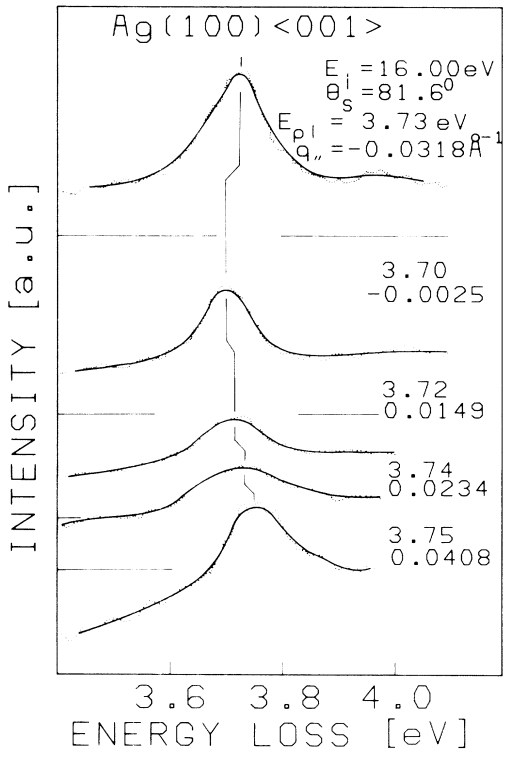

FIG. 1. Sample spectra taken for $E_i=16.00$ eV and at $\theta_s=81.6°$. The data were smoothed by a spline routine. The peak position is determined by a parabolic fit.

measuring plasmon dispersion at low impact energies is angular acceptance α of the EELS, which determines the $q_\parallel$ resolution. α ranges between 1° and 1.5°. A typical set of measurements is reported in Fig. 1 for $E_i = 16.00$ eV and $\theta_s = 81.6°$ along [001] and for crystal at room temperature. The scattering geometry is defined in the inset of Fig. 2. An electron beam of energy E_i is incident upon the sample and is inelastically scattered with an energy $E_f = E_i - E_{pl}$, where E_{pl} is the plasmon energy. From energy and momentum conservation one obtains

$$\hbar q_\parallel = \sqrt{2m}\,(\sqrt{E}\sin\theta_i - \sqrt{E_i - E_{pl}}\sin\theta_s)\,, \qquad (1)$$

where m is the mass of the electron. Loss energy and scattering geometry determine therefore the momentum transfer. The spectra show a single loss with a high-energy tail which is particularly evident for positive $q_\parallel$. Other data were recorded for E_i ranging between 10 and 120 eV and θ_s between 42° and 87°. Only data taken at grazing incidence have, however, enough resolution in $q_\parallel$ to be considered further. Most of the points were recorded along [001]. No dependence was observed on crystal azimuth.[6] Care had to be taken to avoid geometric conditions corresponding to elastic Rydberg resonances[7] as they can strongly deform the shape and shift the position of the loss peak. These points are collected for plasmon energy versus exchanged momentum in Fig. 2. The bars correspond to the $q_\parallel$ resolution which causes an integration over $q_\parallel$. The continuous line was obtained by linear regression best fit between $q_\parallel = 0$ and 0.15 $Å^{-1}$. As one can see the peak maxima disperse linearly upwards in energy with $q_\parallel$ from 3.69 eV with a slope of 1.51 eV/$Å^{-1}$. Beyond 0.15 $Å^{-1}$ the determination of the position of the peaks is less accurate as they broaden considerably because of the opening of efficient damping channels due to interband electron-hole-pair excitation. Note that for vanishing $q_\parallel$ the peak maxima could be shifted upwards in energy because of the integration window. Such an effect is relevant for high impact energies and steep incidence, because of shrinking of reciprocal

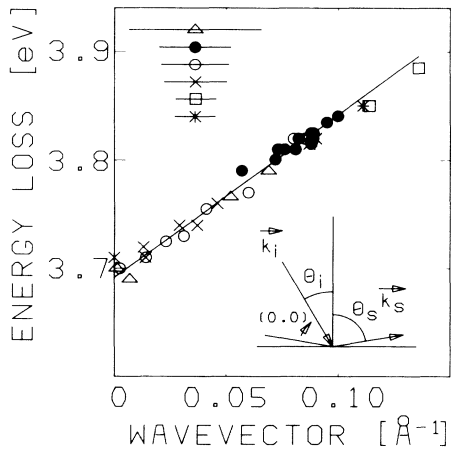

FIG. 2. Collection of the data points vs $q_\parallel$: ×, $E_i = 10.50$ eV, $\theta_s = 86.2°$; ○, $E_i = 16.00$ eV, $\theta_s = 81.6°$; △, $E_i = 16.00$ eV, $\theta_s = 60.0°$; □, $E_i = 38.5$ eV, $\theta_s = 85.8°$; *, $E_i = 76.0$ eV, $\theta_s = 85.2°$; ●, $E_i = 116$ eV, $\theta_s = 85.2°$. ——, linear regression best fit.

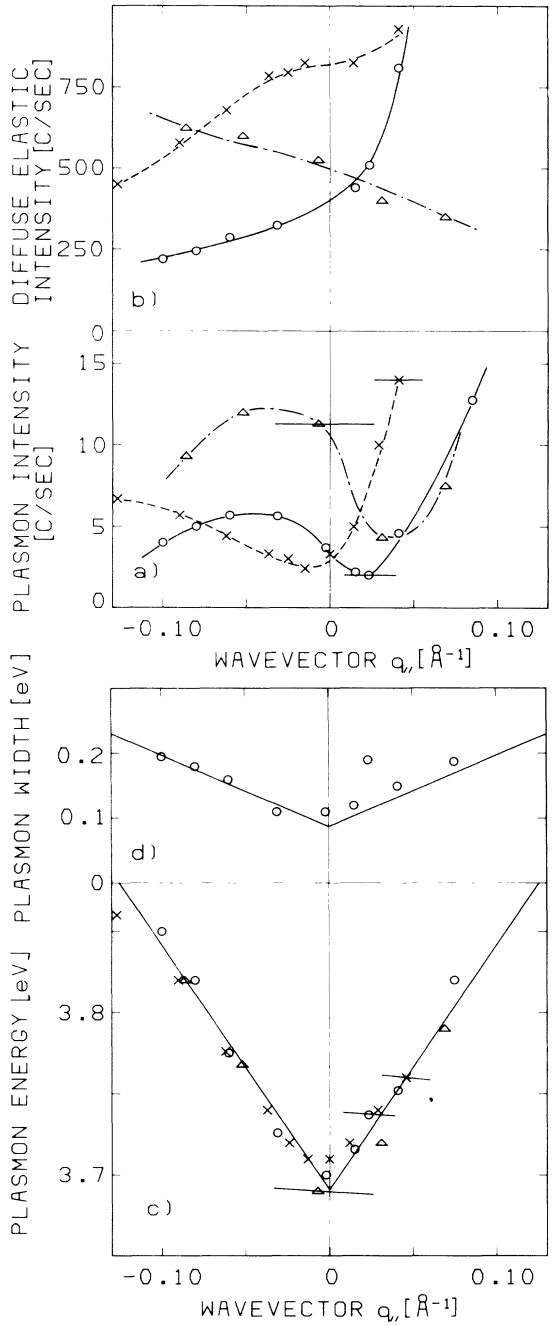

FIG. 3. Set of measurements vs $q_\parallel$: ○, $E_i = 16.00$ eV, $\theta_s = 81.6°$; △, $E_i = 16.00$ eV, $\theta_s = 60.0°$; ×, $E_i = 10.50$ eV, $\theta_s = 86.2°$. (a) The plasmon intensity, (b) the diffuse elastic intensity, (c) the plasmon energy E_{pl}, and (d) full width at half maximum of the plasmon loss. The solid line in (c) is the linear regression best fit as in Fig. 2, elsewhere the lines are only a guide for the eye.

space. For the data reported in Fig. 1, on the other hand, the integration region amounts to $\Delta q_{\parallel}=0.032$ Å^{-1} so that the effect is small except if the inelastic cross section varies strongly on that scale. Although still relevant, our $\Delta q_{\parallel}$ has a grazing incidence strength about half as broad as those reported so far in the literature.[2,3]

In Fig. 3 we report three examples of measurements of intensity and energy as functions of exchanged momentum. They were recorded in the range $q_{\parallel}=\mp 0.10$ Å^{-1}. The three curves show a pronounced minimum for the inelastic intensity [see Fig. 3(a)] while no such a feature is observed for the diffuse elastic intensity [see Fig. 3(b)]. The position of the minimum does not coincide with $q_{\parallel}=0$ as expected for small-angle scattering and dipole interaction.[1] In order to demonstrate that this shift is a physical effect and is not due to a lack in the determination of $q_{\parallel}$, one can take advantage of the symmetry of the dispersion curve with respect to $q_{\parallel}=0$. For the first (open circles) and third (crosses) set of measurements, the error in $q_{\parallel}$ resulted to be less than 0.002 Å^{-1}. These data were reported in Fig. 3 without any correction. For $\theta_s=60.0°$ we obtained an error of 0.007 Å^{-1}. This larger shift is not surprising as under these geometric conditions the $\Delta q_{\parallel}$ window is about twice as large as for grazing incidence. In Fig. 3 these data were therefore shifted in $q_{\parallel}$ by -0.007 Å^{-1}. The loss widths are symmetric with respect to $q_{\parallel}=0$ except for a broadening present at the position of the intensity minima which is particularly evident at $E_i=16.00$ eV and $\theta_s=81.6°$ [see Fig. 3(d)]. This broadening points out to a defocusing mechanism, too.

The shift in position of the minimum cannot be explained in the frame of Refs. 1 and 8 and account must be taken of the interference between incoming and outgoing electron waves and of the phase shift ϕ suffered by the electrons in the scattering off the surface. Following this idea, Persson[9] obtained for the differential inelastic cross section σ of the electron interacting with an adsorbed molecule the following expression:

$$\sigma \propto \frac{k_1}{k_0 \cos\theta_s}\left(\frac{q_{\parallel}}{(k_0-k_1)^2}+\frac{q_{\parallel}\cos\phi}{q_{\parallel}^2+q_{\perp}^2}-\frac{q_{\perp}\sin\phi}{q_{\parallel}^2+q_{\perp}^2}\right)^2, \tag{2}$$

where k_1 and k_0 are the wave vectors associated to the inelastic and to the primary electrons; $q_{\parallel}$ and $q_{\perp}$ are the components of the exchanged momentum parallel and normal to the surface. Equation (2) describes the contribution to the scattering cross section arising from loss-before-reflection and reflection-before-loss processes.[9] The last two terms of the equation take into account that the incoming and outgoing waves interfere with each other in a region near the surface. These contributions were so far neglected since inelastically scattered electrons were studied at not too large angles from the specular beam.

In Fig. 4 we show the behavior of Eq. (2) as a function of $q_{\parallel}$ for the experimental conditions corresponding to the curves of Fig. 3. The phase-shift values reproducing the position of the minima are the following: 0° for $E_i=10.50$ eV, $\theta_s=86.2°$; 5° for $E_i=16.00$ eV, $\theta_s=81.5°$; and 30° for $E_i=16.00$ eV, $\theta_s=60.0°$. The qualitative agreement with the experiment indicates that the explanation is indeed correct, although the dependence of ϕ from θ_s indicates that Eq. (2) is oversimplified and more phase shifts should be taken into account.

This effect may complicate the determination of energy and dispersion of surface plasmons. Because of the

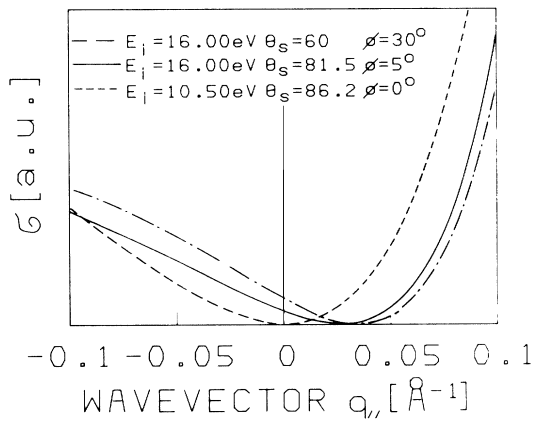

FIG. 4. Plot of σ vs $q_{\parallel}$ as calculated from Eq. (2) for the experimental conditions of the data of Fig. 3. The values of ϕ fitting the positions of the minima are 0°, 5°, and 30° (see text).

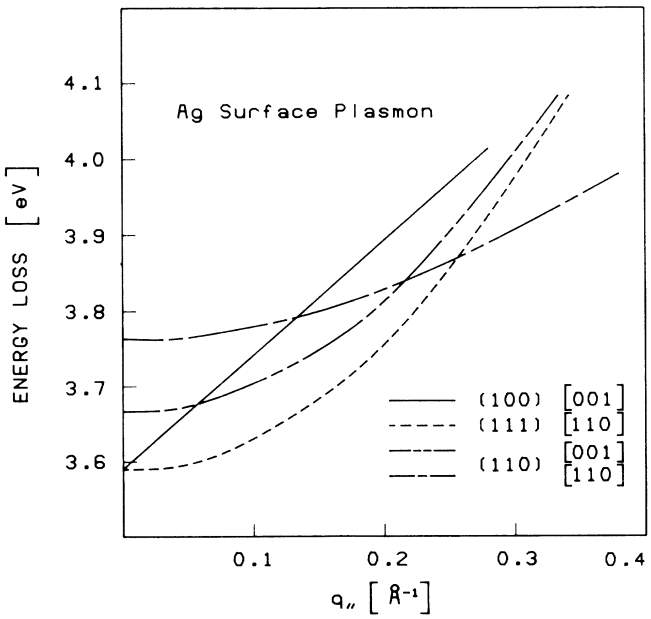

FIG. 5. Comparison between plasmon dispersion on the different low Miller index faces of Ag. Data for (110) and (111) were taken from Ref. 3.

finite window in the $q_\parallel$ space the energy loss may be displaced upwards or downwards in energy depending on the behavior of the cross section with $q_\parallel$. By looking at Fig. 3 it is possible to observe this effect. Near the minimum, in fact, only the side wings contribute to the intensity. The points at $q_\parallel = 0.023$ Å^{-1} (open circles) and at $q_\parallel = 0.040$ Å^{-1} (open triangles) appear broader than the neighbors and are located at somewhat displaced energy than expected from the dispersion curve. In the first case this is clearly caused by the right wing which contributes more than the left one due to the strong anisotropy of the cross section. The opposite occurs in the second case. The same effect is provoked by the asymmetry of the high-energy tail which is present only for positive $q_\parallel$. It is clear that a larger $\Delta q_\parallel$ window may displace the loss position even more. Such features should be, however, associated with a broadening of the losses.

At $q_\parallel = 0$ the experimental width of the surface plasmon is 110 meV. Accounting for momentum resolution, which depends on the steepness of the dispersion relationship and is 48 meV for $\Delta q_\parallel = 0.032$ Å^{-1} and for an energy resolution of 20 meV, we obtain a plasmon width of 95 meV. Cooling the crystal to 140 K reduces the loss width by 10%.

The dispersion curve for Ag(100) is compared in Fig. 5 with those reported for Ag(111) and Ag(110).[3] We note essentially three major facts: (a) Plasmon frequency at vanishing $q_\parallel$ is the same for (111) and (100) faces; (b) (111) and (100) show no azimuthal anisotropy; and (c) the $q_\parallel$ dependence of the dispersion relations is linear in our case but quadratic for Ag(111) and Ag(110).[3] With respect to (a) we believe that the explanation lies in the similarity of the surface electronic spectra of (100) and (111) (Ref. 10) faces which have surface states and $\bar{\Gamma}$ at similar energy above E_F while such a state is absent for (110). Point (b) is an obvious consequence of surface isotropy and confirms the analysis carried out by Suto *et al.*[3] Finally, point (c) is the most intriguing since two different faces of the same material apparently display a qualitative difference in plasmon dispersion. We have no satisfactory explanation for this finding. The difference could be associated with the geometry of the surface. Duke *et al.* do, in fact, report similar dependence for surface-plasmon dispersion on Al(100) and Al(111).[11] Plasmon dispersion on Ag(100) is in accord with the linear relationship derived for free-electron metals by Feibelman[12] and Liebsch[13] at small wave vectors. The slope should then be proportional to the distance of the position of the centroid of the induced charge $d(\omega)$ from the jellium edge according to

$$\omega_s(q_\parallel) = \omega_s[1 - \tfrac{1}{2} d(\omega_s) q_\parallel + O(q_\parallel^2)], \quad (3)$$

where ω_s is the surface-plasmon frequency. In the random-phase-approximation formulation one obtains a positive value for $d(\omega_s)$ and therefore a negative plasmon dispersion. Although jellium theory is not suitable for silver, one can speculate that our positive slope is related to an excess of electrons at the surface, possibly connected to a relaxation of the outer interlayer spacing as suggested also by Korsukov and Lukyanenko[14] for surface-plasmon dispersion on Al. A small relaxation would not be in contrast with the measured phonon spectrum.[5]

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