Evidence for the presence of the multipole plasmon mode on Ag surfaces

F. Moresco and M. Rocca
Centro di Fisica delle Superfici e delle Basse Temperature del CNR and Istituto Nazionale per la Fisica della Materia, Dipartimento di Fisica, via Dodecaneso 33, 16146 Genova, Italy

V. Zielasek, T. Hildebrandt, and M. Henzler
Institut für Festkörperphysik der Universität Hannover, Appelstrasse 2, 30167 Hannover, Germany
(Received 20 September 1996)

Collective surface electronic excitations on Ag(111) and Ag(110) have been studied by energy-loss-spectroscopy LEED. The data allow separation of the contribution to the loss intensity due to monopole and to multipole surface plasmons, thus demonstrating the existence of the latter mode also on noble-metal surfaces. Multipole plasmons are therefore a general property of the optical response of metal surfaces whenever the charge-density profile at the interface is not too abrupt. [S0163-1829(96)51544-4]

Dynamical screening at metal surfaces has been in the foreground of surface investigation for more than 20 years as it influences a large number of physical properties.[1,2] One major breakthrough occurred recently when surface plasmon dispersion on simple metals was studied by angle-resolved low-energy high-resolution electron-energy-loss spectroscopy (HREELS).[3–5] The negative initial slope of the dispersion confirmed the theoretical forecast about the relation of this quantity with the position of the centroid of the screening charge at the surface.[1,6] Moreover multipole plasmon modes were observed,[4] whose existence had been predicted by theory for simple metals years before.[7–9]

The generalization of these results to *d* metals was not straightforward. Ag constituted a particularly well-suited candidate for such study, as it is characterized by a very sharp surface plasmon. The results for the low Miller index Ag surfaces were intriguing[10–16] as the dispersion came out to be positive and dispersion and damping to be anisotropic with respect to crystal face and azimuth. However, for Ag(110) the origin of the azimuthal dispersion anisotropy was ascribed to the quadratic term by Lee *et al.*,[13] and to the linear term by Rocca *et al.*,[12] and for Ag(111) Suto *et al.*[15] excluded the presence of a linear term in the dispersion, contrary to Rocca *et al.*[16] Moreover the data for Ag(111) in Ref. 16 showed an anomalously large spread for the surface plasmon frequency at vanishing momentum transfer $\omega_{sp}(q_{\parallel}=0)$ and the values for surface plasmon damping reported by the different laboratories[10,15,16] differ by a factor of 3. These findings indicate that further investigation of the electronic excitation spectrum of Ag surfaces is necessary, possibly improving the angular acceptance of the spectrometer, which is the most important factor limiting the experimental accuracy.

Such an improvement is now possible by using the recently developed energy resolved spot profile analysis of low-energy electron diffraction (LEED), i.e., a LEED system with both high-momentum and high-energy resolution, also known as energy-loss-spectroscopy low-energy electron diffraction, acronym ELS-LEED.[17] Data on surface electronic excitations obtained with such instrumentation are presented here. As shown elsewhere,[18] they confirm the principal results obtained by our previous HREELS investigations,[12,16] i.e., the positiveness and linearity of the initial dispersion for all Ag surfaces and the anisotropy of the linear dispersion coefficient with respect to crystal face and azimuth. Here we want to show that the better quality of the spectra and the larger experimental basis allows us to highlight the complex nature of the energy-loss peaks near to $q_{\parallel}=0$: apart from the usual monopole surface plasmon our data show evidence also for the presence of the multipole surface plasmon. This discovery is in accord with existing theory,[8,9] which predicts such a mode, whenever the surface-electron-density profile is not too abrupt. Our data demonstrate therefore that the multipole plasmon is a general property of the optical response for Ag and presumably for all metal surfaces. Its existence affects significantly the high frequency optical properties, e.g., it is expected to strongly influence the production of hot electrons by photons, when the frequency matches the one of the multipole mode, ω_{mp}.[19]

For the present experiment the ELS-LEED[17] was tuned to an energy resolution of ≈ 20 meV. The scattering geometry is identical to the one used for spot profile analysis of LEED intensities (SPA-LEED), i.e., near normal incidence and detection (specular reflection occurs at $\theta_i=6°$). The transfer width of the instrument is 1500 Å, which corresponds to a limit in momentum resolution of 0.004 $Å^{-1}$. In ELS-LEED however the resolution is generally limited by the quality of the single crystal under investigation, i.e., by its dislocation induced mosaic structure. The present experiment was performed on a conventional single crystal with (111) orientation and on a dislocation free Ag(110) single crystal. An integration window in reciprocal space $\Delta q_{\parallel}=0.038$ $Å^{-1}$ could be attained for Ag(111), and $\Delta q_{\parallel}=0.021$ $Å^{-1}$ for Ag(110), as determined from the angular FWHM of the specular peak. The latter value of $\Delta q_{\parallel}$ is half as large compared to previous work and is determined by the dislocations created during surface preparation. Even the quality of the data for Ag(111) is, however, better than the one of the previous HREEL work,[16] probably because of the smaller uncertainty in the determination of the scattering geometry.

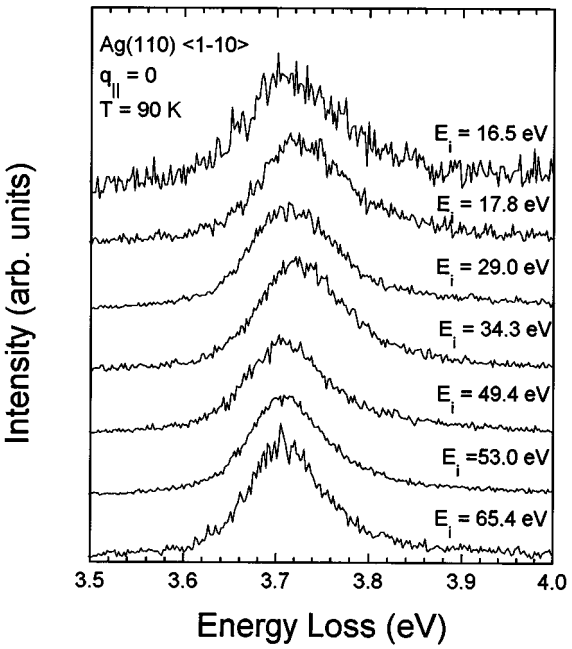

FIG. 1. Energy-loss spectra for Ag(110) recorded with ELS-LEED at $q_{\parallel}=0$ at different impact energies. As one can see, the position of the maximum and the width of the peaks depends on E_i revealing the complex nature of the losses.

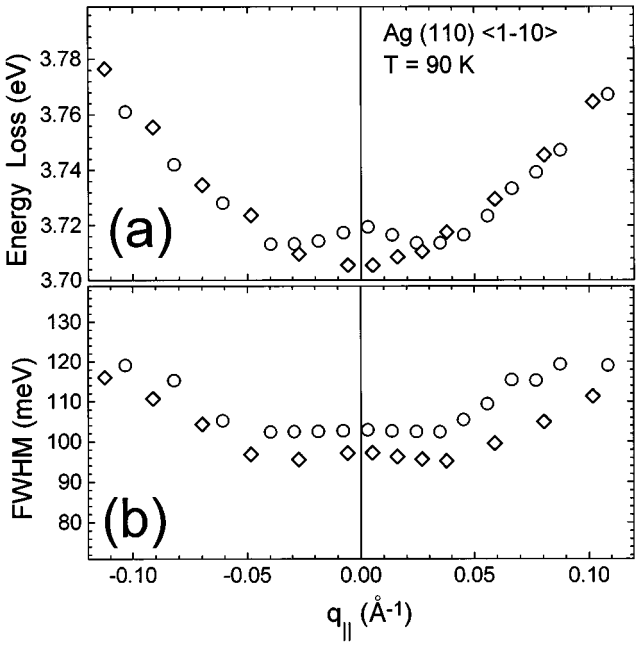

FIG. 2. Collection of (a) the energy losses and (b) the FWHM of the loss peaks vs $q_{\parallel}$ for Ag(110). ELS-LEED data: ◇, $E_i=65.4$ eV; ○, $E_i=16.5$ eV.

Sample spectra recorded for Ag(110) along $\langle 1\bar{1}0\rangle$ at different impact energies E_i, and $q_{\parallel}=0$ are shown in Fig. 1. As one can see in spite of the sharpness of the loss peaks, the position of the maximum and the energetic FWHM depend on E_i. Such behavior is observed also for Ag(111). The energy dependence of the shift indicates that the effect is not instrumental. We conclude therefore that the loss is structured and that the weight of the different components depends on impact energy and scattering geometry. Similar spectra were recorded for other values of $q_{\parallel}$ and allowed to measure the dispersion curve in the usual way by determining the momentum transfer from scattering geometry and energy loss, E_{loss}.[2] Such curves are shown for Ag(110)$\langle 1\bar{1}0\rangle$ in Fig. 2 for two values of E_i, which are denoted by ○ and ◇. As one can see the data points coincide for large $q_{\parallel}$ but deviate significantly near to $q_{\parallel}=0$, where the ◇ behave normally (positive initial dispersion, as found also for other values of E_i and by[12] HREELS), while the ○ are abnormal. As shown in Fig. 2(b) the larger E_{loss} values of the ○ corresponds to a larger FWHM. The anomaly cannot be due to integration over reciprocal space as the slope of the dispersion along Ag(110) is very small and cannot account for a shift of more than a few meV. $\Delta q_{\parallel}$ is, moreover, larger for the case of ◇ than for ○. On the other hand the ○ cannot correspond to the true dispersion as integration over a larger $\Delta q_{\parallel}$ could in no way reduce the FWHM of the loss peaks. Notably the anomaly in the set denoted by ○ occurs at $q_{\parallel}\approx 0$, where the dipole intensity has a minimum.

A similar situation occurs for Ag(111). The maximum of the losses is reported vs $q_{\parallel}$ in Fig. 3(a) for two values of E_i (□ and ◇). Such data are compared with the result of our previous HREELS investigation (× and +).[16] As one can see at small $q_{\parallel}$ E_{loss} depends again on the scattering conditions. This finding cannot be due to different experimental conditions as the sample used in this experiment is the same as in Ref. 16 and was prepared following the same procedure. Again as shown in Fig. 3(b) the FWHM of the losses is largest when E_{loss} is anomalously high. The ELS-LEED losses are moreover broader at $E_i=51.5$ eV than at $E_i=20.1$ eV in spite of the identical

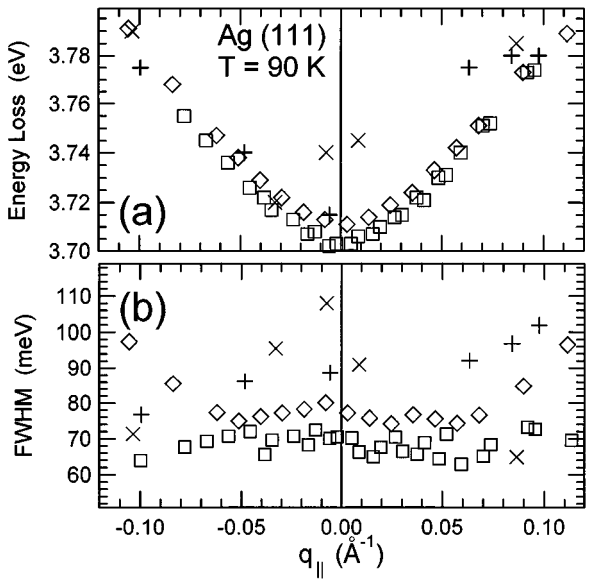

FIG. 3. Collection of (a) the energy losses and (b) the FWHM of the loss peaks vs $q_{\parallel}$ for Ag(111). ELS-LEED data: □, $E_i=20.1$ eV; ◇, $E_i=51.5$ eV; HREELS data (from Ref. 16); +, $E_i=10.7$ eV; ×, $E_i=15.0$ eV.

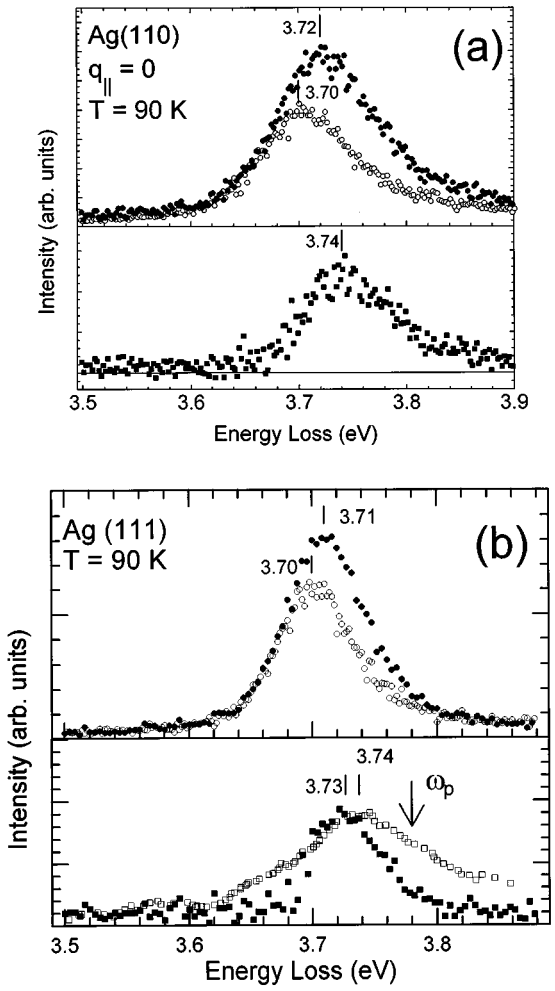

FIG. 4. Upper panels: comparison of the losses observed under different scattering conditions for $q_{\parallel}=0$ for (a) Ag(110) and (b) Ag(111). The spectra are normalized to the low-frequency leading edge. The losses at lower frequency are dominated by the surface plasmon, those at higher frequency contain also a contribution of the multipole mode. Lower panels: difference spectra obtained by subtraction of the spectra in the upper panel. As one can see in both cases a well-defined peak centered at about 3.74 eV is obtained. Such a peak is compared in (b) with the anomalous HREELS spectrum (□) recorded at 15.0 eV and $\theta_s=63.8°$. We believe that such spectrum is dominated by the multipole plasmon. Similar cases were found also for Ag(110).[14] The arrow indicates $\hbar\omega_p=3.78$ eV.

$\Delta q_{\parallel}$. As a side remark let us notice that at $q_{\parallel}=0$ the value of the FWHM for Ag(111) measured by ELS-LEED is the lowest so far reported for all Ag surfaces. Notably, in analogy to the case of Ag(110), the spread in the data is largest near $q_{\parallel}\approx 0$ where the dipole scattering intensity has a minimum. The lowest values of $E_{\rm loss}$ are thereby closest to the optical value ($\epsilon=-1$ at 3.68 eV presumably at 300 K according to Palik[20] and 3.66 eV at T=80 K according to Winsemius[21]).

In the upper panel of Fig. 4 we compare ELS-LEED spectra recorded for $q_{\parallel}\approx 0$ for two different impact energies for (a) Ag(110) and (b) Ag(111). The spectra are normalized to the low-frequency edge of the loss peaks. The difference spectra reported in the lower panels are then obtained by subtraction: in both cases we find a well-defined peak centered at around 3.74 eV. Notably, as shown in Fig. 4(b), the difference spectrum compares nicely with the anomalous HREEL spectrum recorded for Ag(111) at $E_i=15.0$ eV and $\theta_s=63.8°$ (Ref. 16). Peaks at anomalously high frequency were observed with HREELS also for Ag(110) (Ref. 14) and ascribed to the presence of a strong intensity interband transition on the high loss side (excited by impact scattering), not present in the ELS-LEED spectra. No reasonable experimental justification could be found for the case of Ag(111), as reported in Ref. 16. The shift cannot be due to the excitation of the bulk plasmon, as it would be expected at the larger energy[22] $\hbar\omega_p=3.78$ eV [arrow in Fig. 4(b)] while no intensity is present at that $E_{\rm loss}$ value in the difference spectrum. Similarly, it cannot be due to an interband transition as then much broader peaks would be expected (see, e.g., Figs. 1(a) and 1(b) of Ref. 14). Finally, it cannot be due to an elastic reflectivity structure[23] as that effect can be easily discriminated by changing the impact energy.

The relevant excitation must therefore have a frequency in-between $\omega_{\rm sp}$ and ω_p. Such an extra feature for simple metals is the multipole surface plasmon at $\hbar\omega_{\rm mp}$,[24] which was observed by HREELS at $\omega_{\rm mp}\approx 0.8\omega_p$ for alkali metal films[4] and is related to the resonance seen in photoyield measurements from Al.[19] For such a mode the density fluctuation integrates to zero in the normal direction. Its existence for simple metals was the object of a prolonged theoretical debate as it can be sustained by the surface only when the ground state electronic properties are realistically described by using the density-functional scheme.[7,8,19] For Ag its very existence had been questioned because of the extreme closeness of surface and bulk plasmon frequency and because of extra broadening caused by bulk damping processes. No theoretical prediction was, on the other hand, possible, as, e.g., within the model of Liebsch and Schaich[25] Im$[d(\omega)]$ is too steep around 3.74 eV to enable to discern a peak. Experimentally, however, the mode can be evidenced thanks to the different relevant excitation mechanisms, dipole scattering for the surface plasmon and impact scattering for the multipole mode.[26] Interestingly $\omega_{\rm mp}$ lies also for Ag in-between $\omega_{\rm sp}$ and ω_p. The existence of the multipole surface plasmon is in no way specific to Ag and it is expected also for the other metal surfaces as long as the criterion required by theory about the smoothness of the electron density profile is satisfied.

In conclusion we have demonstrated that at hand of new ELS-LEED data a complete picture of the surface excitation spectrum can be obtained for Ag, the previous inconsistencies having to be ascribed to the complex nature of the energy losses that contain, apart from a contribution from the ordinary (monopole) surface plasmon, also the multipole plasmon. The power of the novel method of ELS-LEED for the study of surface electronic excitations is therefore demonstrated and possibilities are opened for the experimental investigation of the rich field of surface electronic excitations.

One of us, F.M., would like to acknowledge the financial support of the Dipartimento di Fisica di Genova for her stay in Hannover and the hospitality of the Hannover group. Scientific discussions with A. Liebsch are acknowledged.

[1] P. J. Feibelman, Prog. Surf. Sci. **12**, 287 (1982).
[2] M. Rocca, Surf. Sci. Rep. **22**, 1 (1995).
[3] K. D. Tsuei, E. W. Plummer, and P. J. Feibelman, Phys. Rev. Lett. **63**, 2256 (1989).
[4] K. D. Tsuei *et al.*, Phys. Rev. Lett. **64**, 44 (1990).
[5] K. D. Tsuei *et al.*, Surf. Sci. **247**, 302 (1991).
[6] A. Liebsch, Phys. Scr. **35**, 354 (1987).
[7] A. J. Bennett, Phys. Rev. B **1**, 203 (1970); C. Schwartz and W. L. Schaich, *ibid.* **26**, 7008 (1982).
[8] J. F. Dobson and G. H. Harris, J. Phys. C **21**, L729 (1988).
[9] J. J. Quinn, Nucl. Instrum. Methods Phys. Res. B **96**, 460 (1995).
[10] R. Contini and J. M. Layet, Solid State Commun. **64**, 1179 (1987); J. M. Layet (private communication).
[11] M. Rocca and U. Valbusa, Phys. Rev. Lett. **64**, 2398 (1990).
[12] M. Rocca, M. Lazzarino, and U. Valbusa, Phys. Rev. Lett. **69**, 2122 (1992).
[13] G. Lee, P. T. Sprunger, and E. W. Plummer, Surf. Sci. **286**, L547 (1993).
[14] M. Rocca and U. Valbusa, Surf. Sci. **287/288**, 770 (1993).
[15] S. Suto *et al.*, Phys. Rev. Lett. **63**, 2590 (1989); M. Rocca, M. Lazzarino, and U. Valbusa, *ibid.* **67**, 3197 (1991); G. Lee *et al.*, **67**, 3198 (1991).
[16] M. Rocca *et al.*, Phys. Rev. B **52**, 14 947 (1995).
[17] U. Scheithauer, G. Meyer, and M. Henzler, Surf. Sci. **178**, 441 (1987); H. Claus, A. Büssenschütt, and M. Henzler, Rev. Sci. Instrum. **63**, 2195 (1992).
[18] F. Moresco, M. Rocca, V. Zielasek, T. Hildebrandt, and M. Henzler (unpublished).
[19] H. J. Levinson, E. W. Plummer, and P. J. Feibelmann, Phys. Rev. Lett. **43**, 952 (1979).
[20] E. D. Palik, in *Handbook of Optical Constants of Solids* (Academic Press, New York, 1985) p. 355.
[21] P. Winsemius *et al.*, J. Phys. F **6**, 1583 (1976).
[22] J. Daniels, Z. Phys. **203**, 235 (1967).
[23] M. Rocca and F. Moresco, Phys. Rev. Lett. **73**, 822 (1994); Phys. Rev. B **50,** 18 621 (1994).
[24] C. Schwartz and W. L. Schaich, Phys. Rev. B **30**, 1059 (1984); K. Kempa and R. R. Gerhardts, Solid State Commun. **53**, 579 (1985).
[25] A. Liebsch, Phys. Rev. Lett. **71**, 145 (1993); **72**, 789 (1994); P. Feibelman, *ibid.* **72**, 789 (1996); A. Liebsch and W. L. Schaich, Phys. Rev. B **52**, 14 219 (1995).
[26] This was also the case for simple metals (see the HREELS intensities reported in Ref. 5). Also in that case the multipole mode was generally less intense than the ordinary surface plasmon except near $q_{\parallel}=0$ where the dipolar cross section has a minimum.