Surface-plasmon dispersion and multipole surface plasmons in Al(111)

Gennaro Chiarello, Vincenzo Formoso, Anna Santaniello,* Elio Colavita, and Luigi Papagno
Istituto Nazionale di Fisica della Materia and Dipartimento di Fisica, Università della Calabria, 87036 Arcavacata di Rende, Cosenza, Italy

(Received 13 July 2000)

We have measured the collective electronic excitations of the Al(111) surface by means of angle-resolved high-resolution electron-energy-loss spectroscopy. Loss spectra reveal both the monopole and the multipole surface plasmons. The measured dispersion of the monopole surface plasmon is negative, as predicted by calculations of the dynamic response of the electron at the surface of a free-electron-like sample. The aluminum multipole surface plasmon, which was not detected in previous electron-energy-loss investigations, is clearly observed in present spectra.

Dynamical screening of electrons at metal surfaces to an external time-dependent probe has attracted much attention[1] because it influences many physical properties. Simple metals have been treated theoretically using the jellium model in order to describe important effects such as the energy transfer between incident particles and substrate and the excitation of normal modes of electrons at the surface.[2]

Detailed density-functional-response calculations predict that two collective surface modes exist at the surface of a simple metal:[2,3] the ordinary surface plasmon,[4] which has a monopole character perpendicular to the surface, and the so-called multipole surface plasmon[2,5,6] characterized by the fact that the integral of the electronic density perpendicular to the surface is zero. Both modes have been found experimentally[7] at the surface of alkali-metal films by electron-energy-loss spectroscopy (EELS). Those early measurements also confirmed the negative dispersion of the surface plasmon predicted by the theory.[2]

According to theoretical studies,[2] the dispersion of the surface plasmon is related to the position $d(\omega_s)$ of the centroid of the induced electronic charge. The energy dispersion of the surface plasmon is given by the relation[2,7]

$$\omega_s(q_\parallel)=\omega_s(0)\left[1-\frac{q_\parallel d(\omega_s)}{2}\right], \tag{1}$$

where $\omega_s=\omega_p/\sqrt{2}$ and ω_p is the bulk plasma frequency given by the expression $\omega_p=\sqrt{4\pi ne^2/m}$, where n is the density of electrons in the bulk of the material and m is the mass of the free electron. If $d(\omega_s)$ is outside the jellium edge (positive value of d), as $q_\parallel$ increases, less electrons per unit volume experience the plasmon electric field, resulting in a lower surface plasmon frequency[7] (negative dispersion); if $d(\omega_s)$ is inside the jellium, (negative value of d), as $q_\parallel$ increases much more of the plasmon electric field overlaps the region of high electron density of the metal, resulting in a higher surface-plasmon frequency (positive dispersion).

The good agreement between theory and experiments found for alkali-metal films[7] was not confirmed by measurements performed on high-density metals such as aluminum. The surface-plasmon dispersion of Al surfaces was measured by inelastic low-energy electron diffraction (ILEED) investigations.[8] The results showed a negative initial dispersion slope in Al(100) and a positive one in Al(111). Data from high-energy-loss experiments[9] on Al thin films indicate a positive dispersion. More recent electron-energy-loss measurements[10] on Al(111) were unable to solve the intriguing problem because the data showed no clear linear and negative initial dispersion. Moreover, the same EELS measurements[7,10] on Al(111) did not show the multipole mode and the result was ascribed to the very low cross section of this nondipole mode. As possible explanation of the above results, it has been also suggested[1] that the collective excitations of Al surfaces could be influenced by lattice effects, which are usually neglected in calculations. Some theoretical[11] works have, indeed, shown that a proper description of the dynamical response of Al requires the inclusion of band-structure effects.

This state of the art calls for new experimental investigations in order to establish if dielectric properties of Al surfaces contain features ascribed to lattice effects or if the observed discrepancies are of mere experimental nature. The aim of this Report is to present high-resolution electron-energy-loss (HREELS) measurements of the electronic excitations of Al(111). Our results give clear and unambiguous

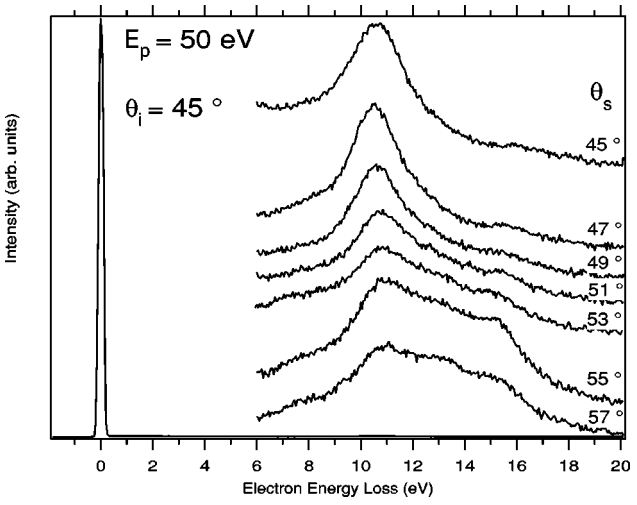

FIG. 1. Energy-loss spectra of Al(111) at different scattering angles θ_s. The incident angle is $\theta_i=45^0$ and the primary energy beam is 50 eV.

 ©2000 The American Physical Society

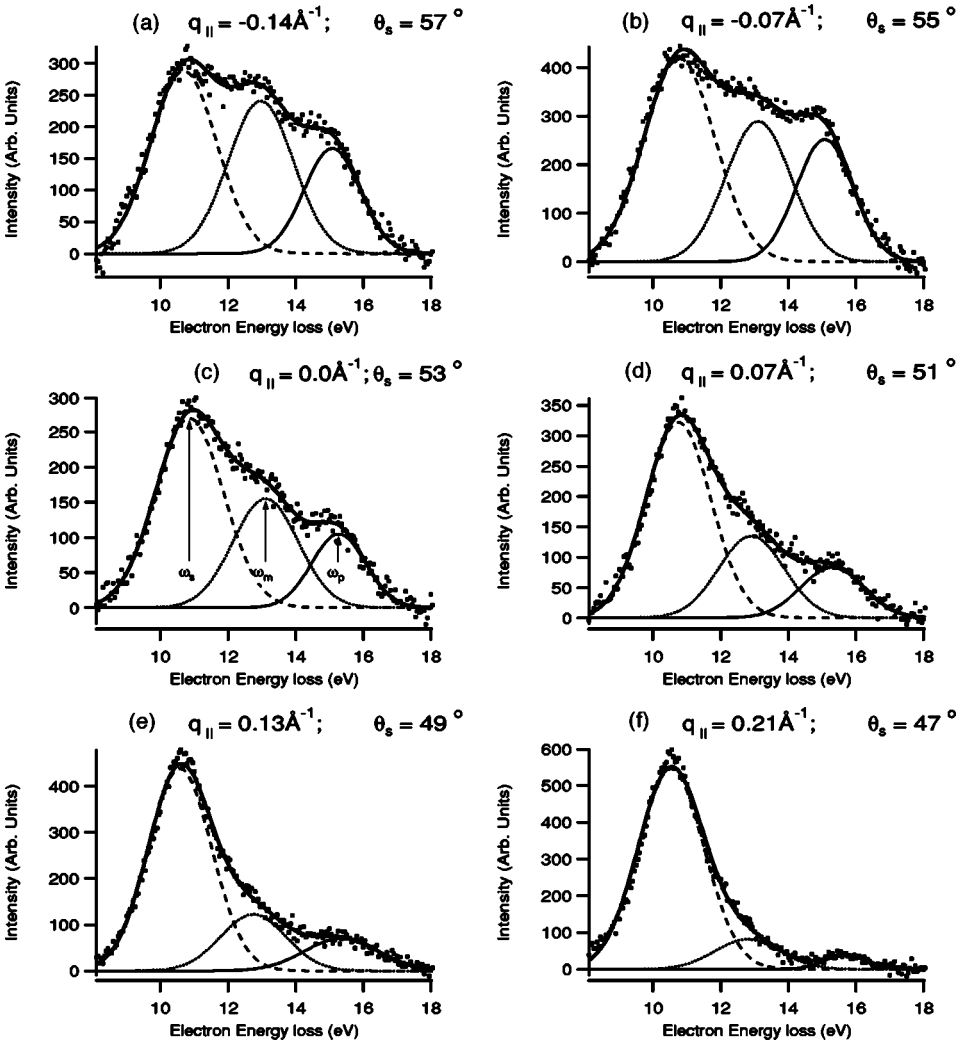

FIG. 2. Loss spectra at different scattering angles after background subtraction. The solid line is the fitting curve of the spectrum. ω_s, ω_m, and ω_p represent the surface plasmon, the surface multipole plasmon, and the bulk plasmon, respectively.

evidence that the surface-plasmon dispersion curve is negative, in agreement with the prediction of the jellium model for simple metals. Furthermore, loss spectra taken at small parallel momentum transfer, $q_{\parallel}$, reveal the presence of the multipole surface plasmon, thus supporting the observation of recent photoyield experiments.[12]

The electronic excitations of Al(111) were measured in an ultrahigh-vacuum system (base pressure 5×10^{-11} Torr) equipped with standard facilities for surface characterization.[13] The spectrometer consists of two 50-mm spherical deflectors with a collection angle of $\pm1°$. The energy resolution of the spectrometer was degraded to 180 meV in order to increase the signal-to-noise ratio for off-specular spectra. All measurements have been made at room temperature. The crystal was prepared by cycles of Ar^+ bombardment and annealing at 750 K until no impurity traces could be seen on the surface as monitored by Auger and x-ray photoemission (XPS) spectroscopies. The Al(111) surface showed an excellent LEED pattern characterized by sharp spots and very low background. We paid much care to the surface cleanliness, since it was shown that the surface-plasmon dispersion may change sign by adsorption[14] of an adlayer. The EELS measurements were carried out with an incident electron energy of 50 eV and an incident angle of 45° with respect to the surface normal. The dispersion of the surface plasmon was obtained by moving the analyzer around the specular direction while keeping the crystal and the monochromator in a fixed position. The primary electron beam is inelastically scattered with an energy $E=E_i-\hbar\omega$, where $\hbar\omega$ is the loss energy. The momentum transfer parallel to the surface $q_{\parallel}$ is given by

$$\hbar q_{\parallel}=\sqrt{2m}[\sqrt{E_i}\sin\theta_i-\sqrt{E_i-\hbar\omega}\sin\theta_s]. \qquad (2)$$

Owing to the finite angular acceptance of the analyzer, each spectrum taken at a certain scattering angle integrates within a window in $q_{\parallel}$ space given by

$$\delta q_{\parallel}=\sqrt{2m}[\sqrt{E_i}\cos\theta_i-\sqrt{E_i-\hbar\omega}\cos\theta_s]\delta\theta_s, \qquad (3)$$

where $\delta\theta_s$ coincides with the angular acceptance α of the analyzer.[15] Thus, if the angular acceptance is smaller than the width of the dipole cone, as in the present experiment, $\hbar q_{\parallel}$ represents the experimental resolution in **q** space. A good $q_{\parallel}$ resolution is obtained by using a low primary-electron beam energy, but the condition $\hbar\omega\ll E_i$, valid for the dipole scattering regime, must be fulfilled. The primary electron energy used in the present experiment was a good compromise among $q_{\parallel}$ space resolution, dipole scattering approximation, and surface sensitivity.

Curves in Fig. 1 show loss spectra of the Al(111) surface recorded at different scattering angles. The loss spectrum

obtained in the specular geometry is characterized mainly by a single peak at 10.55 eV and is related to the ordinary surface plasmon. For off-specular scattering angles two other features arise in the loss spectra, and the surface-plasmon exhibits a clear energy dispersion.

The energy and width of the surface plasmon and of the other collective excitations were obtained after background subtraction and fitting of the experimental loss spectra. The result of this procedure is shown in Fig. 2. It is worthwhile to pay attention to the fact that non-dipole-active modes (the multipole surface plasmon[7]) are better observed for small values of momentum transfer $q_{\parallel}$. Loss spectra could easily be fitted by three Gaussian line peaks. The peak at the highest loss energy in the spectrum of Fig. 2(c) (about 15.34 eV) corresponds to the excitation of the Al bulk plasmon. We note that, with an incident electron beam of 50 eV, the bulk plasmon is not very intense in the spectrum taken in the specular direction (Fig. 1). In contrast, in loss spectra obtained for an incident beam energy of 30 eV, the bulk-plasmon excitation is well evident even in specular spectra. The third peak (13.20 eV) in Fig. 2(c), located between the bulk- and the surface-plasmon losses, is the multipole plasmon. We find that at $q_{\parallel}=0$ the energy of this feature is about $0.87\omega_p$, as expected.[5]

The surface multipole mode has been theoretically predicted[2,5,6] but never observed before in an electron-energy-loss experiment on Al surfaces.[7] However, it has been observed in a recent angle- and energy-resolved photoyield experiment on Al(111).[12] Present EEL measurements and published photoyield data give the same energy for the multipole mode but a different full width at half maximum (FWHM). In fact, we find (at $q_{\parallel}=0$) a FWHM of 2.1 eV against 3 eV measured by photoyield experiments. The reasons for these differences are not yet clear. With our measurements, however, we are inclined to give more importance to the scattering geometry, which appears to be necessary to enhance the multipole plasmon over bulk contributions. On the other hand, at $q_{\parallel}=0$, we find that the intensity of the multipole mode is about 57% of that of the surface plasmon and is even more intense than the bulk plasmon. Many factors may influence the excitation of the multipole plasmon, but since it is a genuine surface mode,[5] the scattering geometry and the choice of the energy of the incident beam may play an important role and may be crucial for its detection. Measurements are in progress to verify its existence also in Al thin films.

Figure 3(a) displays the energy of the surface plasmon as a function of $q_{\parallel}$ over a range of $q_{\parallel}$ from -0.2 Å^{-1} to $+0.6$ Å^{-1}. The bars show the integration window in the **q** space due to the angular resolution of the analyzer. The surface-plasmon dispersion is negative up to 0.2 Å^{-1}, then the loss energy increases and the dispersion becomes positive. As expected,[1] the dispersion curve shows symmetric behavior with respect to $q_{\parallel}=0$, supporting the data obtained by the fitting procedure of the spectra. The solid line was drawn through the points by using a fourth-order polynomial curve to stress the behavior of the dispersion. At small $q_{\parallel}$, the surface-plasmon energy decreases from 10.86 eV ($q_{\parallel}=0$) to 10.55 eV ($q_{\parallel}=0.2$ Å^{-1}). Due to the small variation of the surface-plasmon energy with respect to the width of the three losses in the spectra, some discussion has to be made in order to ascertain whether the observed negative dispersion is a genuine dispersion or rather a result of superposition of different resonances. If an interference effect exists, it should be more important for spectra taken at $q_{\parallel}\leqslant 0$, where a strong multipole contribution is present as can be observed in Figs. 2(a) and 2(b). For these two spectra the presence of the multipole peak slightly shifts the experimental surface-plasmon peak to higher loss energies with respect to the values obtained by our fitting procedure. On the other hand, for $q_{\parallel}>0$, the multipole mode is less important and its

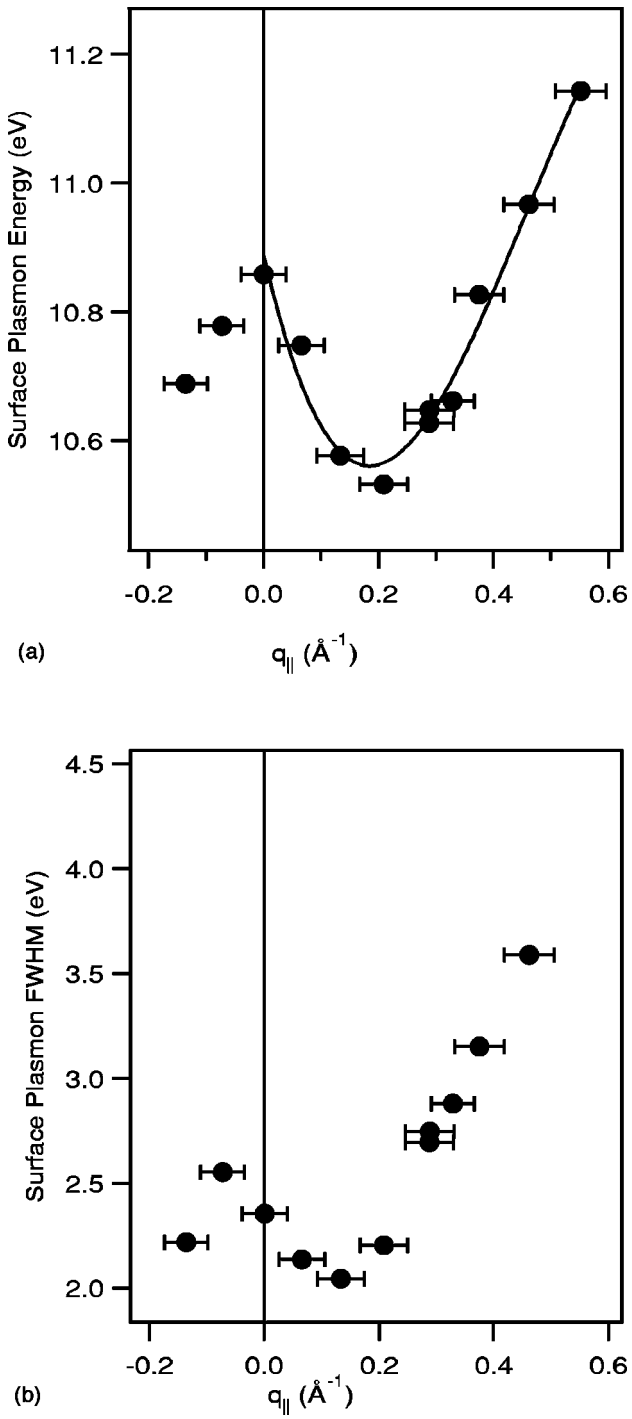

FIG. 3. (a) Surface-plasmon energy as a function of $q_{\parallel}$ for Al(111). (b) Surface-plasmon full width at half maximum as a function of $q_{\parallel}$ for Al(111).

presence does not affect the energy of the surface plasmon in Figs. 2(c)–2(f). If we plot the surface-plasmon peak energy without any fitting procedure versus $q_{\parallel}$, we obtain a qualitative similar curve as the one shown in Fig. 3(a), confirming the negative energy dispersion that we obtained in a more accurate analysis of the experimental data. The full width at half maximum of the surface plasmon versus $q_{\parallel}$ is reported in Fig. 3(b). Data seem to indicate a weak negative initial dispersion followed by an increase of the surface-plasmon width. At $q_{\parallel}=0$ we find a FWHM of 2.3 eV in good agreement with the reported value of $0.15\omega_p$.[7] A negative initial dispersion of the FWHM was also reported for Ag(110) (Refs. 15 and 16), Mg(0001) (Ref. 17), and graphite (Ref. 18). Interestingly, the FWHM curve has a behavior similar to the $q_{\parallel}$ dependence of the surface-plasmon loss of Fig. 2, suggesting a physical link between these two quantities as already demonstrated in a recent theoretical work.[19]

In conclusion, we report on the experimental evidence of the initial negative dispersion of the surface-plasmon loss of the Al(111) surface as predicted by theory within the jellium approximation for small wave vector $q_{\parallel}$ transfer. Furthermore, we give clear evidence that the multipole mode of aluminum surfaces is detectable by angle-resolved high-resolution electron-energy-loss spectroscopy measurements.

This work was funded by the Italian MURST (COFIN 97 021178261003) and by a special project of CNR.

*Permanent address: Sincrotrone Trieste S.C.p.A, 34012 Trieste, Italy.

[1] M. Rocca, Surf. Sci. Rep. **22**, 1 (1995).
[2] P.J. Feibelmann, Phys. Rev. Lett. **30**, 975 (1973); Prog. Surf. Sci. **12**, 287 (1982).
[3] A. Liebsch, Phys. Rev. Lett. **71**, 145 (1993); **72**, 789 (1994).
[4] R.H. Ritchie, Phys. Rev. **106**, 874 (1957).
[5] J. Sellares and N. Barberan, Phys. Rev. B **50**, 1879 (1994).
[6] J. Dobson and G.H. Harris, J. Phys. C **21**, 2729 (1988).
[7] K.D. Tsuei, E.W. Plummer, A. Liebsch, K. Kempa, and P. Bakshi, Phys. Rev. Lett. **64**, 44 (1990); K.D. Tsuei, E.W. Plummer, and P.J. Feibelmann, *ibid.* **63**, 2256 (1989).
[8] C.B. Duke, L. Pietronero, J.O. Porteus, and J.F. Wendelken, Phys. Rev. B **12**, 4059 (1975).
[9] K.J. Krane and H. Rather, Phys. Rev. Lett. **37**, 1355 (1976).
[10] See data on Al(111) reported in Ref. 1.
[11] A. Fleszar, A.A. Quong, and A.G. Eguiluz, Phys. Rev. Lett. **74**, 590 (1997).
[12] S.R. Barman, H. Haberle, and K. Horn, Phys. Rev. B **58**, R4285 (1998).
[13] G. Chiarello, A. Cupolillo, A. Amoddeo, L.S. Caputi, L. Papagno, and E. Colavita, Phys. Rev. B **55**, 1376 (1997).
[14] J.S. Kim, L. Chen, L.L. Kesmodel, P.G. Gonzales, and A. Liebsch, Phys. Rev. B **56**, R4402 (1997).
[15] M. Rocca, F. Biggio, and U. Valbusa, Phys. Rev. B **42**, 2835 (1990).
[16] M. Rocca and U. Valbusa, Surf. Sci. **287/288**, 770 (1993).
[17] P.T. Sprunger, G.M. Watson, and E.W. Plummer, Surf. Sci. **269/270**, 551 (1992).
[18] P. Laitenberger and R.E. Palmer, Phys. Rev. Lett. **76**, 1952 (1996).
[19] L. Yibing, A.C. Levi, and M. Rocca, Surf. Sci. **336**, 371 (1995).