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Plasmon of Shockley surface states in Cu(111): A high-resolution electron energy loss spectroscopy study

A. Politano, G. Chiarello,* V. Formoso, R. G. Agostino, and E. Colavita
Dipartimento di Fisica and CNISM, Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia,
Università degli Studi della Calabria, 87036 Rende (Cs) Italy

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High-resolution electron energy loss spectroscopy was used to investigate the low-energy collective excitations of the Cu(111) surface. Measurements showed a collective mode with an energy of 1.1 eV. The measured dispersion of the plasmon mode was negative. We suggest that this mode arises from the oscillation of electrons confined to the Cu(111) surface within quasi-two-dimensional Shockley surface states. Moreover, we show that the acousticlike mode theoretically proposed for the (111) surface of noble metals is not observed in copper. The behavior of the plasmon dispersion curve and the lack of the acoustic mode call for specific theoretical interpretations of the present experimental results.

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In recent years, the strong influence of surface electronic states on a variety of physical phenomena occurring at surfaces, such as adsorption and diffusion, has attracted much interest.[1–5] The (111) surfaces of noble metals exhibit a large confined gap within the projected bulk band structure centered at the $\bar{\Gamma}$ point of the surface Brillouin zone.[6–8] Electronic states of different origin can exist in this gap. They may be Shockley surface states[8] or states induced by adsorbates (quantum wells).[9–12] Electrons occupying these states are confined in the two-dimensional top layer of the bulk sample. While the free-electron nature of the Shockley surface states have been confirmed using angular resolved photoemission,[8] to the best of our knowledge, no evidence exists to demonstrate that such confined electrons can support collective modes.

Recently, Silkin *et al.*[13] calculated the dynamical response of the (111) surfaces of Cu, Ag, and Au to a longitudinal perturbation. Considering the coexistence of surface states with bulk states, calculations point to an acoustic surface plasmon with a frequency that shows linear-acoustic-like dispersion at small wave vectors.[13–16] The excitation of a two-dimensional collective mode was found in the $(\sqrt{3}\times\sqrt{3})$-Ag/Si(111) surface using electron backscattering measurements.[17] The Ag overlayer was assumed to form a nearly-free-electron-like band which is well separated from the bulk bands.

In principle, the Shockley states of the Cu(111) surface are an ideal system for investigating the collective excitations of electrons confined within a quasi-two-dimensional space. The response of this system to a longitudinal perturbation has not yet been studied, especially with regard to the coexistence of Shockley states with three-dimensional bulk states.

High-resolution electron energy loss spectroscopy (HREELS) is particularly suitable for investigating collective excitations[18] due to its wide accessible range (0–0.5 Å^{-1}) of parallel momentum transfer and to its high energy resolution (1–10 meV). HREELS was thus used to investigate the dielectric response of the Cu(111) surface under grazing incidence with high energy resolution in angular-resolved mode.

We report the observation of a plasmonic mode of Cu(111) with an energy of 1.1 eV and show that the dispersion of this collective mode is negative. Experimental evidence is presented which proves that the centroid of the induced electronic charge distribution of this plasmon mode lies outside the surface of Cu. In light of the present results, the theoretical model regarding the nature of collective excitations at the (111) surface of noble metals[13] should be reconsidered.

HREEL experiments were performed using an electron energy loss spectrometer (Delta 0.5 by SPECS) operating at a base pressure of 5×10^{-9} Pa. Loss spectra were recorded at grazing geometry with an incident angle of 65° with respect to the surface normal. Electron beam energies were varied in the range of 12–100 eV while the energy resolution of the spectrometer was degraded to 10 meV so as to increase the signal-to-noise ratio for off-specular spectra. The angular acceptance (α) of our electron analyzer was ±1°. Dispersion of the collective mode, i.e., $E_{loss}(q_{\parallel})$, was measured by moving the analyzer while keeping the sample and the monochromator in a fixed position.

A Cu(111) crystal with a purity of 99.9999% was used. The surface was cleaned by repeated cycles of ion sputtering and annealing at 800 K in a preparation chamber (base pressure 3×10^{-8} Pa). Surface cleanliness and order were checked using low energy electron diffraction (LEED) and Auger electron spectroscopy measurements carried out using a hemispherical analyzer (Phoibos 100 by SPECS). The Cu (111) surface exhibited an excellent LEED pattern, which was characterized by sharp spots and a very low background. The sample was oriented along the $\bar{\Gamma}$-$\bar{\mathrm{M}}$ direction and all measurements were made at room temperature, although HREEL spectra recorded at 150 K gave the same results.

Figure 1 shows HREEL spectra acquired in specular geometry and as a function of the primary electron beam energy. Loss spectra showed a peak at 1.1 eV, and the onset of collective excitations of valence electrons could be detected at higher energies, above 2.1 eV. The intensity of the loss peak at 1.1 eV was quite low, but it could be reliably measured and was reproducible. In the loss region close to the elastic peak where an acoustic plasmon is expected[13] no excitation was observed, as shown in Fig. 2. Two-dimensional

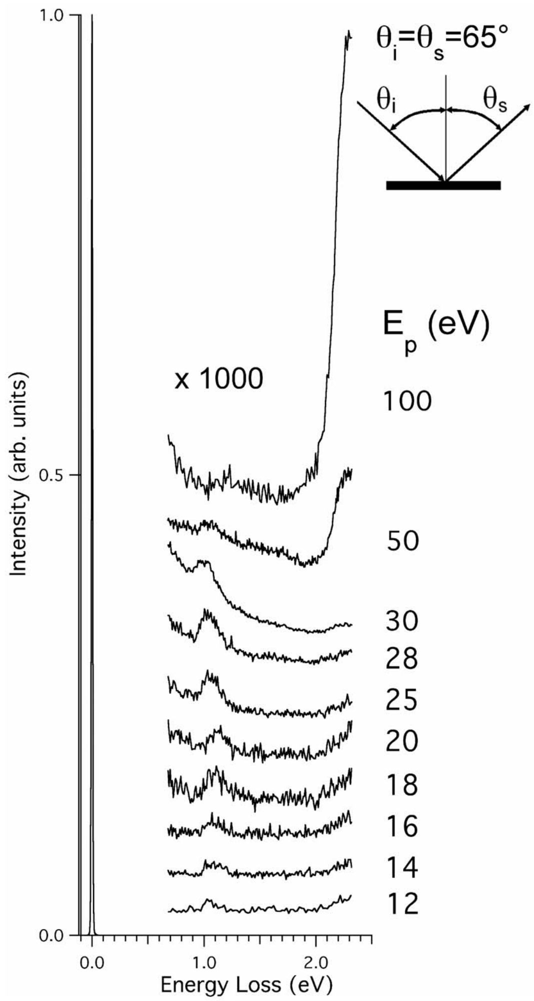

FIG. 1. Electron energy loss spectra of a Cu(111) surface as a function of the electron beam energy E_p at 300 K. All spectra were recorded in specular geometry with an incident angle of $\theta_i=65°$ with respect to the sample normal.

acoustic plasmons are expected to be excited by the dipole mechanism.[17] In particular, for Cu(111) at small parallel momentum transfer such a collective mode should be located at loss energies close to the elastic peak.[13] Actually, no excitation was observed in specular and off-specular geometry (Fig. 2) below 1.1 eV, although the experimental apparatus was set up to enable us to excite the dipole collective mode with an expected very low cross section. Such finding excludes in our opinion the presence of any acoustic plasmon in Cu(111).

Changing the energy of the primary electron beam E_p slightly modifies the loss energy of the observed peak. On the contrary, the cross section for the excitation of this mode undergoes dramatic changes when varying E_p. In fact, around $E_p=25$ eV the intensity of this loss feature reaches its maximum, while a bulklike contribution begins to predominate only when E_p is at least 50 eV. At $E_p=100$ eV, collective bulk excitations become the only contribution to the HREEL backscattering yield.

Inspection of the surface band structure[6,7] of Cu(111) does not support the existence of electron-hole (*e-h*) optical transitions from occupied bulk states to empty surface states at about 1.1 eV. The high surface sensitivity offered by the grazing incidence of the electron beam makes it possible to confidently define the surface character of the peak at 1.1 eV. We thus suggest that the peak at 1.1 eV (Fig. 1) represents the collective longitudinal charge oscillation of electrons confined in two-dimensional Shockley surface states. The possibility that the peak might be an acoustic plasmon of Cu(111) cannot be excluded, although the theoretical value proposed by Silkin *et al.*[13] is much lower than 1.1 eV. The behavior of the dispersion curve of this surface excitation should allow for the discrimination of an acoustic plasmon from a collective mode that reflects the presence of nearly free electrons in Shockley surface states.

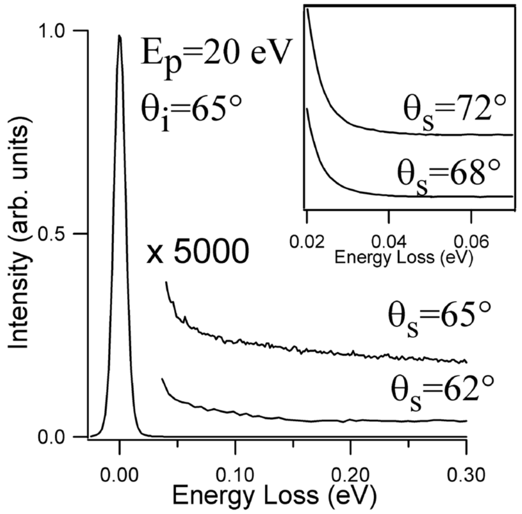

FIG. 2. Electron energy loss spectra for specular and off-specular geometry. The inset shows the region close to the elastic peak for two more off-specular spectra.

To measure plasmon dispersion, values for the parameters E_p, impinging energy, and θ_i, the incident angle, were chosen so as to obtain the highest signal-to-noise ratio. The primary beam energy used for the dispersion, $E_p=20$ eV, provided, in fact, the best compromise among surface sensitivity, the highest cross section for mode excitation, and $q_\parallel$ resolution. As

$$\hbar \vec{q}_\parallel = \hbar\,(\vec{k}_i \sin\theta_i - \vec{k}_s \sin\theta_s),$$

the parallel momentum transfer $q_\parallel$ depends on E_p, E_{loss}, θ_i, and θ_s according to

$$q_\parallel = \frac{\sqrt{2mE_p}}{\hbar}\left(\sin\theta_i - \sqrt{1-\frac{E_{loss}}{E_p}}\,\sin\theta_s\right)$$

where E_{loss} is the energy loss and θ_s is the electron scattering angle.[18]

Accordingly, the integration window in reciprocal space[19,20] is

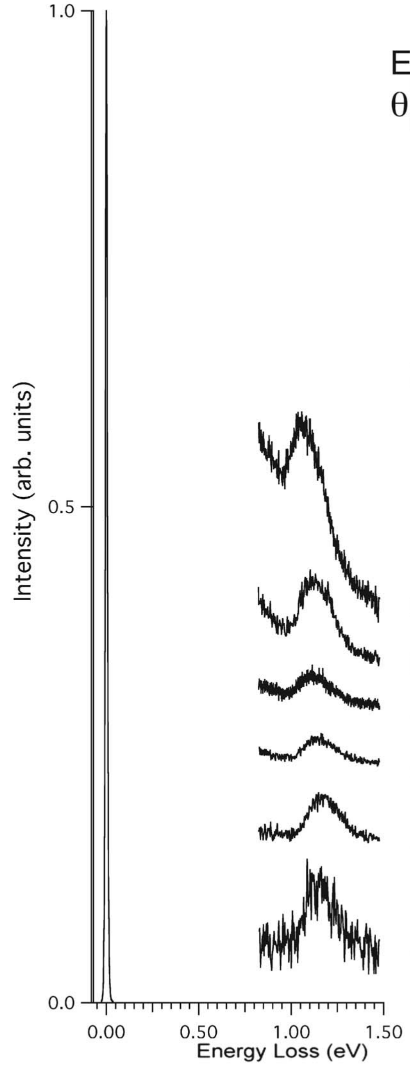

FIG. 3. Electron energy loss spectra of Cu(111) at different scattering angles θ_s. The incident beam energy E_p is held constant at 20 eV and all spectra were recorded at an incident angle of $\theta_i = 65°$ with respect to the sample normal.

$$\Delta q_{\parallel} \approx \frac{\sqrt{2mE_p}}{\hbar}\left(\cos\theta_i + \sqrt{1-\frac{E_{loss}}{E_p}}\cos\theta_s\right)\alpha$$

where α is the angular acceptance of the apparatus.[18] Under the conditions in the present experiment, we estimate $\Delta q_{\parallel} = 0.035$ Å^{-1}.

Figure 3 shows the raw loss spectra. Because of the very low number of counts at the peak maximum, the spectra could not be analyzed beyond $q_{\parallel} \approx 0.17$ Å^{-1}. An exponential background was subtracted from each curve and the maximum $E_{loss}(q_{\parallel})$ of each resulting curve was determined using a trial best-fit Gaussian line shape. The intensity of the backscattering yield around 1.1 eV versus the off-specular angle clearly demonstrates that the plasmon mode is dipolar in nature because it is peaked in the specular direction.[18]

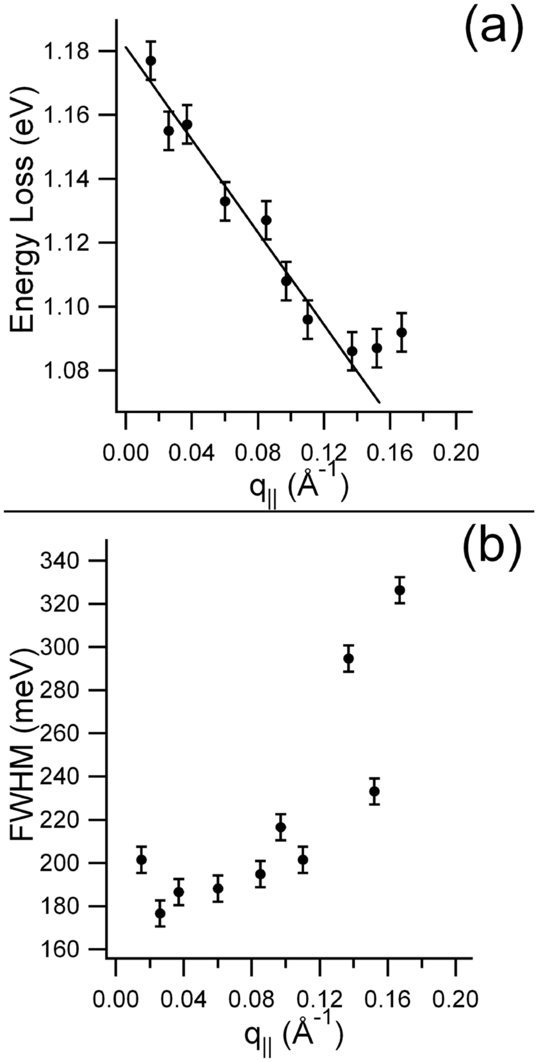

FIG. 4. (a) Cu(111) Shockley plasmon energy as a function of $q_{\parallel}$. (b) Full width at half maximum of the Cu(111) Shockley plasmon peak as a function of $q_{\parallel}$.

Figure 4(a) shows that the dispersion curve $E_{loss}(q_{\parallel})$ is negative with respect to $q_{\parallel}$. Within experimental error and up to $q_{\parallel} = 0.13$ Å^{-1}, the dispersion curve exhibits a linear profile such that $E_{loss}(q_{\parallel}) = a + bq_{\parallel}$ where $a = 1.181$ eV and $b = -0.724$ eV Å. The measured data diverge from a linear behavior in the range between 0.13 and 0.17 Å^{-1}, and a local minimum at $q_{\parallel} = 0.15$ Å^{-1} can be inferred.

These HREEL measurements support neither the recent theoretical predictions[13] (acousticlike dispersion) nor the behavior expected for a two-dimensional free-electron gas (i.e., square root dispersion).[21] The dispersions of the ordinary monopole surface plasmon of Al(111),[22] of alkali-metal surfaces,[23] and of thin alkali-metal layers on metal substrates[24] are known to be negative. Moreover, it is dependent, at small $q_{\parallel}$, on the position of the centroid of the induced electronic charge density associated with the surface plasmon field.[18,25,26] Similarly, the negative slope of the present dispersion curve may indicate that the collective mode is of analogous physical nature and that the centroid of the induced plasmonic charge lies outside the Cu(111) surface. Although this conclusion needs theoretical support, we tentatively suppose the spatial extension of the Shockley states of the Cu(111) surface similar to that of a thin free-electron metal layer deposited on a metal substrate. On the other hand, the charge density probability of Shockley states is peaked at the surface and decays exponentially toward the solid coexisting with bulk states. This interpretation would explain the negative slope of the present dispersion curve, but would not give any suggestion for the absence of the predicted acoustic plasmon.

The damping of the plasmon excitation is clearly revealed by the trend of the full width at half maximum (FWHM) versus $q_{\parallel}$, as shown in Fig. 4(b). This behavior is similar to that found on other metal surfaces.[22] The width of the Cu(111) plasmon initially decreased, followed by a steep increase as a function of $q_{\parallel}$. At $q_{\parallel} > 0.026$ Å^{-1} electrons may be promoted from occupied bulk states to unoccupied surface states[13] such that the corresponding plasmon peak would broaden considerably until decaying into the single-particle excitation continuum.

In conclusion, the loss measurements presented in this paper provide evidence of the existence of a collective mode related to Cu(111) Shockley surface states centered at the $\bar{\Gamma}$ point of the surface Brillouin zone. The dispersion curve of this plasmon mode exhibits a linear negative dependence on the transfer momentum parallel to the surface. Furthermore, neither the plasmon energy nor its dispersion concur with existing theoretical predictions. Electronic coupling between surface states and three-dimensional bulk states should have an important role in calculating collective excitations on clean (111) surfaces of noble metals. As a matter of fact, interactions between surface states and substrate states are considerable in thin metallic overlayers deposited on semiconductor or metal surfaces because the tail of the surface state wave function can interact with the substrate. While HREEL experiments on electrons confined in similar surfaces of other noble metals are currently under way, these findings provide the grounds for theoretical studies aimed at characterizing the excitation mode presented here.

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*Corresponding author. Electronic address: chiarello@fis.unical.it

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