OFFPRINT

Acoustic surface plasmon on Cu(111)

K. Pohl, B. Diaconescu, G. Vercelli, L. Vattuone, V. M. Silkin, E. V. Chulkov, P. M. Echenique and M. Rocca

EPL, 90 (2010) 57006

Please visit the new website

www.epljournal.org
TARGET YOUR RESEARCH WITH EPL

Sign up to receive the free EPL table of contents alert.

www.epljournal.org/alerts
Acoustic surface plasmon on Cu(111)

K. Pohl\textsuperscript{1(a)}, B. Diaconescu\textsuperscript{1(b)}, G. Vercelli\textsuperscript{2}, L. Vattuone\textsuperscript{2}, V. M. Silkin\textsuperscript{3,4,5}, E. V. Chulkov\textsuperscript{3,4}, P. M. Echenique\textsuperscript{3,4} and M. Rocca\textsuperscript{2}

\textsuperscript{1} Department of Physics and Materials Science Program, University of New Hampshire - Durham, NH 03824, USA
\textsuperscript{2} CNISM, IMEM-CNR and Dipartimento di Fisica, Università di Genova - Genova, Italy, EU
\textsuperscript{3} Departamento de Física de Materiales and CFM (CSIC-UPV/EHU), Facultad de Ciencias Químicas, Universidad del País Vasco - Apdo. 1072, 20080 San Sebastián/Donostia, Spain, EU
\textsuperscript{4} Donostia International Physics Center (DIPC) - P. Manuel Lardizabal 4, 20018 San Sebastián/Donostia, Spain, EU
\textsuperscript{5} IKERBASQUE, Basque Foundation for Science - 48011 Bilbao, Spain, EU

received 13 April 2010; accepted in final form 1 June 2010
published online 5 July 2010

PACS 73.20.Mf – Collective excitations (including excitons, polarons, plasmons and other charge-density excitations)

PACS 71.45.Gm – Exchange, correlation, dielectric and magnetic response functions, plasmons

PACS 73.20.At – Surface states, band structure, electron density of states

Abstract – Contrary to previous reports we show that the acoustic surface plasmon (ASP) exists also at noble-metal surfaces, thus demonstrating the generality of this phenomenon in the presence of partially filled Shockley surface states. Angle-resolved high-resolution electron energy loss spectroscopy measurements and calculations of the surface loss function indicate that for Cu(111) the ASP is a sharp feature up to a loss energy of about 0.4eV. The dispersion is indeed linear (acoustic) with a slope (sound velocity) of $(4.33 \pm 0.33)$ eV\textdegree{}A in good agreement with recent theoretical predictions. The ASP can play important roles down to the meV regime, precluded to ordinary surface plasmons, for electron, phonon and adsorbate dynamics, as well as chemical reactions and advanced microscopies.

Copyright © EPLA, 2010

Introduction. – How solids interact with their environment depends in a significant, and often crucial way on the properties of their surfaces. Sometimes the effect of truncation of a crystal is limited to small modifications of its bulk properties, but very frequently, the surface introduces new phenomena which cannot be deduced from the knowledge of the properties of extended systems only. It has been known for a long time that the presence of the surface can introduce new intrinsic electronic states, usually referred to as Tamm and Shockley surface states \cite{1,2}. These states, whose wave functions are localized at the surface, are of great interest in surface science due to their relevance in many phenomena and have been subject of intensive theoretical and experimental study for years. A well-known example of such states is a $sp$ surface state at the (111) surface of noble metals. It has a partly occupied free-electron–like parabolic dispersion and it is frequently considered as a prototype of a quasi–two-dimensional (2D) electron gas, with a 2D Fermi energy equal to the surface state binding energy at the center of the surface Brillouin zone. On the other hand, this 2D electron gas overlaps in the surface region with the three-dimensional (3D) bulk electrons and, actually, constitutes only a small fraction of the total charge density in the vicinity of surface atomic layers. Nevertheless, due to their 2D character and slower decay into the vacuum in comparison with the bulk states, the surface states play an important role in many phenomena which take place at metal surfaces. Recently, it was demonstrated that they can dramatically affect the low-energy dynamical screening properties of surfaces, providing a mechanism for the existence of a novel phenomenon – collective charge density oscillations involving \textit{out of phase} fluctuations between the surface and bulk electronic subsystems with a peculiar linear energy dispersion at small 2D momenta —the acoustic surface plasmon (ASP) \cite{3}.

Very recently this mode was discovered on the bare (0001) surface of bulk beryllium \cite{4}. The observation was in stark contrast to the common understanding that such low-energy plasmons could only be excited in spatially
separated layered plasmas found in more exotic layered structures [5], like in strictly 2D systems [6] as well as in quantum-well heterojunctions [7]. A recent study by Traverse et al. also reports the observation of low-energy collective modes on noble-metal nanoparticles, and suggests that they may be of similar plasmonic nature [8]. Such low-energy collective excitation modes with acoustic dispersion should have a strong influence on the dynamics near the Fermi level. The ASP corresponds to the appearance of broad band dynamical long-range charge density oscillations at metal surfaces [9] in addition to the well-known static Friedel oscillations [10–12]. Once created somewhere on the surface, the ASP charge density wave can propagate along the surface with a phase velocity that is, due to its sound-like dispersion, the same as its group velocity. Hence, a signal consisting of several ASP waves can, in principle, propagate along the surface without distortion.

In this paper, we show that contrary to previous investigations [13–16] and even dedicated reports [17], such low-energy collective excitations can also exist on the (111) surface of copper, thus proving that the existence of ASPs is indeed a general phenomenon. The ASP owes its existence to the interplay of the bulk electron gas with surfaces that support a partially occupied surface state in the same region of space and thus should be common to metal surfaces that support a partially occupied surface state band within a wide bulk energy gap [3,18]. Its dispersion is mainly determined by the Fermi velocity of the surface state, \( v_F^{2D} \), and follows closely the upper edge of the continuum for electron-hole (e-h) pair excitations within the surface state band; although to be a well-defined excitation it should disperse above this continuum [19].

**Experiment.** – The experiments were performed in an ultrahigh vacuum apparatus at a base pressure of about \( 1 \times 10^{-10} \) mbar, equipped with an angle-resolved high-resolution electron energy loss (HREEL) spectrometer [20]. In most measurements the energy resolution was set to about 15 meV, in order to improve the signal-to-noise ratio and be able to acquire the inelastic loss state binding energy in this temperature interval [21]. This observation is in agreement with the only small variation of the surface state binding energy in this temperature interval [21].

Figures 1(a) and (b) show HREEL spectra taken at different electron energies \( E_i \) and scattering angles \( \theta_s \).

\[
q_I = \frac{\sqrt{2m}}{\hbar} \left( \sqrt{E_i \sin \theta_i} - \sqrt{E_i - E_{\text{loss}} \sin \theta_s} \right),
\]

along the \( \Gamma-M \) direction for both positive and negative values of the momentum transfer parallel to the surface \( q_I \) (by changing the electron’s angle of incidence \( \theta_i \)). The acquisition time was about 2 hours per spectrum.

A loss peak is observed to disperse as a function of the electron’s parallel momentum \( q_I \). The energy loss maximum of the dispersing peak, \( E_{\text{loss}} \), in each EEL spectrum was then used to compute the corresponding \( q_I \) for the ASP based on the conservation of energy and momentum in the scattering process [13],
where $E_i$ ($E_s = E_i - E_{loss}$) and $\theta_i$ ($\theta_s$) are the incident (scattered) energy and angle of the incident (scattered) electron. The finite angular acceptance of the instrument $\alpha$ translates into a finite integration window over momentum space [13],
\[
\Delta q_{\parallel} = \frac{\sqrt{2m}}{\hbar} \left( \sqrt{E_i \cos \theta_i - \sqrt{E_i - E_{loss} \cos \theta_s} \alpha} \right). \tag{2}
\]

The last relation was used to compute the integration window over the momentum transfer parallel to the surface, i.e. for an angular acceptance $\alpha$ of the instrument ranging from 2° to 7° full width at half-maximum. The broad shape of the measured ASP is a conjugate effect of the natural width of the ASP and of $\alpha$ [4]. Due to the acoustic behavior of the ASP, the scan curve and the dispersion intersect at a small angle causing the finite integration of the spectrometer to translate into a relatively large integration over the energy loss for the positive momentum transfer. For negative momentum transfer the energy integration is significantly smaller due to an intersection close to 90°. The narrow dipole lobe, however, results then in a low excitation probability and thus in a much weaker ASP signal. The experimentally determined energy loss peak could be followed up to 1 eV as shown in fig. 2.

The dispersion is clearly not affected by changing the kinematic parameters in the scattering process, such as $E_i$ and $\theta_s$. As expected, in the long-wavelength limit the energy of the new mode approaches zero linearly for vanishing values of the momentum transfer parallel to the surface. The measured sound velocity or slope of the dispersion intersect at a small angle causing the finite integration of the spectrometer to translate into a relatively large integration over the energy loss for the positive momentum transfer. For negative momentum transfer the energy integration is significantly smaller due to an intersection close to 90°. The narrow dipole lobe, however, results then in a low excitation probability and thus in a much weaker ASP signal. The experimentally determined energy loss peak could be followed up to 1 eV as shown in fig. 2.

To confirm that the ASP is indeed connected with the presence of a Shockley surface state, we suppressed the latter by adsorbing 0.25 monolayers (ML) of oxygen [22,23]. Comparing HREEL spectra taken before and after O$_2$ exposure in the bottom panel of fig. 1 gives clear evidence of the dramatic decrease in the ASP intensity.

**Comparison with theory.** – The close-packed surfaces of the noble metals Cu, Ag, and Au, as well as Be(0001) support a partially occupied surface state close to the Fermi level. These quasi-2D bands are strongly localized near the surface and show a mainly parabolic, almost free-electron-like dispersion with 2D wave vector around the $\Gamma$ point, thus forming a 2D electron gas overlapping with the 3D bulk electrons. Recently we have shown that this interplay between the partially occupied 2D band and the 3D bulk electron continuum is responsible for the ASP. This novel phenomenon is mainly driven by the fact that the non-local character of the dielectric function prevents the ASP from being screened out by the 3D bulk states [4].

Silkin et al. have predicted that the non-local screening model which strictly includes the partially occupied surface state is a very general mechanism [18]. Their self-consistent calculations of the surface response function of the (111) surfaces of Cu, Ag, and Au, by considering a one-dimensional model to describe the surface band structure, show that the sound velocity of the ASP is very close to the Fermi velocity $v_F^{2D}$ of the 2D surface state bands. The calculated ASP dispersion for Cu(111), shown as a solid black line in fig. 2, is in good agreement with the experimental data. The apparent slight deviation at higher values of the momentum transfer is likely to be caused by the simplicity of the 1D model which

![Acoustic surface plasmon on Cu(111)](image)

**Fig. 2:** (Color online) Maxima of the electron energy loss features. (a) The experimental data were obtained from the integration window of the EEL spectrometer in momentum space and to the uncertainty in the location of the peak’s maxima. The black dashed lines represent a least-square linear fit to all data points for negative and positive $q_\parallel$ and considering the error intervals for both $E_{loss}$ and $q_\parallel$. The black solid and black dotted lines depict the theoretical ASP dispersion and the upper edge of the e-h pair continuum calculated within the 1D model in ref. [18], respectively, while the shaded area shows the ab initio e-h pair continuum compiled from ref. [24]. (b) Scattering geometry in EEL spectra measurements. (c) Surface Brillouin zone of Cu(111).
assumes a free-electron–like, parabolic dispersion for the surface state. Inclusion of an \textit{ab initio} surface state dispersion, which deviates slightly from the free-electron–like case in the higher range of $q_{\|}$ provides a more realistic description. As a consequence, the upper edge of the \textit{e-h} pair continuum moves down from the dotted line in fig. 2(a), derived within the 1D potential model, to the top of the gray area calculated from first-principles density functional theory [24]. A future \textit{ab initio} calculation is therefore expected to show that the improved theoretical ASP dispersion decreases accordingly, because it follows very closely the upper edge of the continuum for \textit{e-h} pair excitations within the surface state band. This has been shown to be the case in our recent study of Be(0001) where the inclusion of the full surface band structure from first-principles calculation moved down in energy both the ASP dispersion and the 2D \textit{e-h} pair continuum thus significantly improving the agreement between experiment and theory [4].

The theoretical value for the Fermi velocity of the \textit{ab initio} surface state band is about 0.28 eV $\cdot$ h in Cu(111) [24] and 0.37 eV $\cdot$ h in Be(0001) [4], i.e. in Cu(111) it is about 25\% smaller than in Be(0001). This difference is reflected in the shallower dispersion of the ASP measured on Cu(111) of (4.33 ± 0.33) eVÅ compared to the slope measured on Be(0001) of (5.83 ± 0.25) eVÅ [4]. The intensity of the ASP is strongly influenced by the position of the surface state at $\Gamma$, the center of the surface Brillouin zone, with respect to the bottom of the energy gap formed by the surface-projected bulk bands. For Cu(111) the energy difference between the surface state and the bottom of the energy gap is about 0.5 eV [25] compared to 1.5 eV for Be(0001) [26] causing the ASP on Cu(111) to be weaker than on Be(0001).

Calculations predict the copper ASP to be well defined up to $\sim$0.4 eV [18], whereas in the present experiment the loss becomes broader with $q_{\|}$ and is still present up to almost 1 eV. In fig. 3 we show the calculated surface loss function, $\text{Im}[g(q_{\|},\omega)]$, of Cu(111) as a function of energy along two lines in the momentum-energy phase space corresponding to the second and the fifth spectrum of fig. 1(a) (thick solid lines). In the same figure we also show curves representing the surface loss function calculated along the mentioned experimental scans and smoothed with Gaussians of different broadenings for momenta $\Delta q_{\|}$ and energy $\Delta_{\omega}$. One can see that at small $q_{\|}$ and energy in fig. 3(a) the calculated ASP peak results in a rather sharp energy loss (which does not arise in the case of the calculated $\text{Im}[g(q_{\|},\omega)]_{\text{SS}}$ for a hypothetical free-standing surface state system), whose profile is significantly affected by the scan line and by the broadening. On the other hand, the broad calculated peak structure in fig. 3(b) has its origin in incoherent \textit{e-h} pair transitions within the surface state and does not correspond to any collective mode. This feature has a prominent peak on the upper energy side which corresponds to the broad peak features seen in the experimental spectra at energies above $\sim$0.4 eV. Notice how in fig. 3(b) at energies below 0.77 eV it resembles the \textit{e-h} pair peak in $\text{Im}[g(q_{\|},\omega)]_{\text{SS}}$.

\textbf{Conclusions.} – In summary, in the present HREEL measurements we have observed the low-energy ASP mode on the Cu(111) surface, thereby giving experimental confirmation that this kind of collective electronic excitation is a general phenomenon on metal surfaces that support a partially occupied surface state within a wide bulk energy gap. It is caused by the non-local screening of the surface electrons due to bulk electrons. Due to its low energy and sound-like (acoustic) dispersion character such a mode is expected to play an important role in electron, phonon and adsorbate dynamics, as well as chemical reactions with energies down to a few meV.

We experimentally observed the ASP on the Cu(111) surface in the energy range up to $\sim$0.4 eV in good agreement with theoretical prediction. Additionally we found broad peaks in the EEL spectra at higher energies which we can attribute to signals from the upper border of \textit{e-h} pair excitations within the surface state. The observation of the ASP on a noble-metal surface is remarkable, since such surfaces are important for physical, chemical, and biological investigations. The possibility to excite dynamical charge density waves related to ASP in a controlled way might introduce an exciting perspective in these fields. Thus the ability to displace atomic species at metal
surfaces due to static Friedel oscillations was recently demonstrated [27–30]. On the other hand, potentially much more powerful ASP charge oscillations [9] might revolutionize the manipulation procedures at the surfaces once a controlled way of their use will be found. We believe that indeed ASPs are excited in many dynamical processes at metal surfaces, but up to now escaped its clear identification due its rather fast velocity.

***

This work was supported in parts by the National Science Foundation under Grants No. DMR-0134933 and DMR-0753467. We acknowledge partial support from the University of the Basque Country (Grant No. GIC07IT36607), the Departamento de Educación del Gobierno Vasco, and the Spanish Ministerio de Ciencia y Tecnología (MCyT) (Grant No. FIS200766711C0101).

REFERENCES