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Low-energy bulk plasmon of nickel

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ABSTRACT

High-resolution electron energy loss spectroscopy has been used to study low-energy bulk excitation modes of planar-bound electrons (bulk plasmons) in nickel. We observed for the first time a bulk plasmon at about 1.2 eV, in agreement with dielectric theory. The behavior of its amplitude with the off-specular angle ensures the dipolar nature of such mode. On the other hand, the intensity of the plasmon peak is vanishing upon ion bombardment due to the sputtering-induced modification of dielectric function.

1. Introduction

Plasmons are longitudinal normal modes of charge fluctuation in a metallic sample excited by an external electromagnetic field [1–5]. Time-dependent density-functional theory reasonably describes collective electronic excitations in simple metals (alkali metals, Al). However, available theoretical models are not able to completely describe electromagnetic excitations in more complex systems (transition metals). In particular, the presence of d electrons and the subsequent s-d polarization [6] has a strong influence on the dynamical response at the surface. Thus, investigation of electronic response of transition-metal systems is required in order to understand dynamical screening of electromagnetic fields at metal surfaces and the influence of band structure on surface electronic excitations.

Collective electronic excitations have been experimentally investigated over a variety of different systems by means of different spectroscopic techniques [6–8]. The bulk loss function, probed by high-resolution electron energy loss spectroscopy (HREELS), could be defined in terms of the dielectric function $\varepsilon(\mathbf{q}, \omega)$ as [9,10]:

$$f = -\mathrm{Im}\left(\varepsilon^{-1}\right) = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} \tag{1}$$

where ε_1 and ε_2 are the real and the imaginary part of the dielectric function, respectively.

For small $\boldsymbol{q}$ (with respect to the reciprocal lattice vectors of the system), the loss function in (1) could be obtained in terms of the optical dielectric function, $\varepsilon(0, \omega)$ as the dependence of ε on $\boldsymbol{q}$ could be neglected.

In Ref. [11] it was demonstrated that minima of the $-f''$ function (the second derivative of f changed of its sign) correspond to absorption peaks while each maximum to a peak in the surface loss function.

In particular, in recent years low-energy collective excitations at single-crystal metal surfaces are attracting a considerable interest [12–15] as their small frequency allows them to participate in many dynamical processes involving electrons and phonons and, moreover, they also should influence the decay rate of all electronic excitations at the metal surface and also influence chemical reactions [12]. It has been suggested that the formation of Cooper pairs in high-transition-temperature superconductors [16] could be mediated by low-frequency plasmons. Furthermore, they could be used as sensors for detection of chemical and biological species [17].

2. Experimental

Measurements have been performed in ultra-high vacuum conditions, with a base pressure of 5×10^{-9} Pa. The substrate is a single-crystal of Ni(111). The surface was cleaned by repeated cycles of ion sputtering and annealing at 1000 K. Sample cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively. The Ni(111) surface after the annealing procedure showed an excellent LEED pattern characterized by sharp spots

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against a very low background. The reference EELS spectrum is related to this condition.

Also vibrational measurements have been used for monitoring surface cleanliness.

HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS) with an angular acceptance of ±1°. Loss spectra were acquired with a primary electron beam energy ranging between 20 and 50 eV. The incident angle with respect to the sample normal was fixed at 55°. The energy resolution of the spectrometer was degraded to 10 meV so as to increase the signal-to-noise ratio of loss peaks.

All measurements have been performed at room temperature. Measurements have been carried out in a few minutes in order to minimize the contamination of the Ni(111) surface by CO molecules [18].

It is worth remembering that the parallel momentum transfer $q_{\parallel}$ is defined [8,13] as:

$$q_{\parallel} = \frac{\sqrt{2mE_p}}{\hbar}\left(\sin\alpha_i - \sqrt{1-\frac{E_{\mathrm{loss}}}{E_{\mathrm{p}}}}\sin\alpha_S\right) \quad (2)$$

where m is the mass of the electron, E_{p} is the energy of the impinging electron beam, E_{loss} is the loss energy, and α_{i} and α_{s} are the incident and scattering angles.

3. Results and discussion

3.1. Comparison of experiment with dielectric theory

HREELS experiments on Ni(111) showed the presence of a peak around 1.2 eV. Fig. 1 shows a comparison between our own experimental results with calculations of the electronic response of nickel by the Full Potential Linear Muffin Tin Orbitals (FPLMTO) *ab initio* method (see Ref. [10] for more detail).

The centroid of the peak revealed in HREELS experiments (centered around 1.2 eV) nearly coincides with the maximum of $-f''$ obtained by calculations. The agreements is excellent even if it is worth remembering that a perfect coincidence is not mathematically possible.

According to the theoretical framework developed in Ref. [11] this finding is a clear evidence of the plasmonic nature of the feature at 1.2 eV. We assign it to a plasmon of electrons in the valence band of Ni(111). On the other hand, the presence of a minimum in $-f''$ around 0.5–0.7 eV should correspond to a strong absorption process. Ultraviolet [19] and soft x-ray angle-resolved photoemission [20] experiments showed the presence of symmetry-allowed single-particle transitions $\Delta_1 \rightarrow \Delta_1$ and $\Delta_1 \rightarrow \Delta_5$ in bulk Ni.

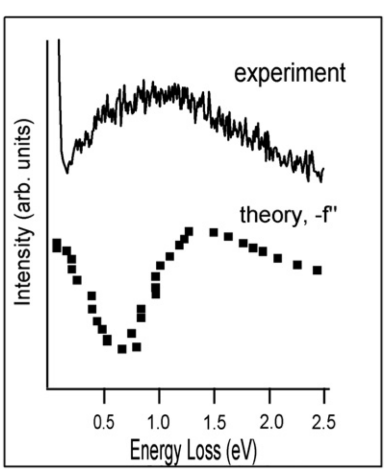

Fig. 1. (top) HREEL spectrum of the Ni(111) surface acquired at a primary energy of 40 eV and for $\alpha_{\mathrm{i}} = \alpha_{\mathrm{s}} = 55°$. The parallel momentum transfer associated to the peak at 1.2 eV in these experimental conditions is 0.015 Å^{-1}. (bottom) Second derivative, changed of its sign, of the theoretical loss function of Ni calculated by FPLMTO *ab initio* method (data taken from Ref. [10]).

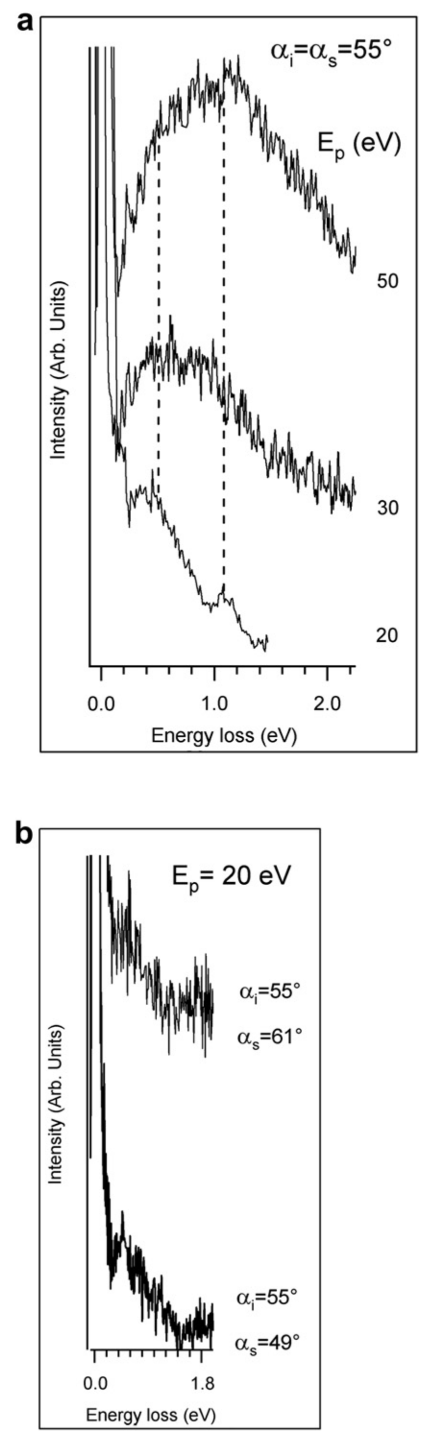

Fig. 2. a: HREEL spectra of the Ni(111) surface as a function of the impinging energy. b: HREEL spectra of the Ni(111) surface acquired with a primary energy of 20 eV as a function of the scattering angle. The incident angle is fixed at 55°.