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Induced charge-density oscillations at metal surfaces

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Abstract

Induced charge-density (ICD) oscillations at the Cu(1 1 1) surface caused by an external impurity are studied within linear response theory. The calculation takes into account such properties of the Cu(1 1 1) surface electronic structure as an energy gap for three-dimensional (3D) bulk electrons and a s–p_z surface state that forms two-dimensional (2D) electron system. It is demonstrated that the coexistence of these 2D and 3D electron systems has profound impact on the ICD in the surface region. In the case of a static impurity the characteristic ICD oscillations with the $1/\rho^2$ decay as a function of lateral distance, ρ, are established in both electron systems. For the impurity with a periodically time-varying potential, the novel dominant ICD oscillations which fall off like $\sim 1/\rho$ are predicted.

Keywords: Surface electronic phenomena; Noble metals; Low index single metal surfaces; Electronic surface states; Adsorbates

In the last years, scanning tunneling microscopy has become a powerful tool to study phenomena governed by screening at metal surfaces, i.e., charge rearrangement in response to the disturbance caused by impurities or defects [1–10]. Remarkable examples of that are the visualization of surface-state-originated Friedel oscillations of the induced charge-density (ICD) at metal surfaces [1,2] and the investigation of the indirect long-range interaction between adsorbates mediated by these oscillations [11]. It has been demonstrated [12,13] that at noble-metal (1 1 1) surfaces this interaction, whose energy decays as $1/\rho^2$ with the lateral distance ρ between adsorbates, can lead to mutual redistribution of adsorbed atoms up to $\rho \sim 10$ nm. This interaction might also be responsible for the rearrangement of adsorbate species on the Si(1 1 1)-$\sqrt{3} \times \sqrt{3}$-Ag surface [14]. Moreover, very recently it has been reported on a realization of a self-assembled two-dimensional (2D) atomic structure due to this interaction [15].

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In the theoretical studies of such phenomena, the scattering approach has found the wide application [12,16–18]. Within this approach, a s–p$_z$ surface state at the noble-metal (1 1 1) surfaces is considered to form a 2D free electron gas, ignoring the fine structure of the surface-state wave function and the fact that this 2D electron gas *coexists* with underlying three-dimensional (3D) electron system. It is well known that the 2D electron system responds to the introduction of an impurity by producing Friedel oscillations with the characteristic $1/\rho^2$ decay [19], whereas in the 3D electron gas the oscillations fall off as $1/R^3$, R being a distance from the impurity [20]. Nevertheless, up to date, the question of how the 2D and 3D systems respond *simultaneously* in the vicinity of a metal surface has not been addressed yet. An answer can be obtained, in principle, from ab initio calculations. But, at present, these evaluations are feasible only for systems with the lateral distances between adsorbates of the order of several Å [21].

In this letter we investigate the response of an electron system at a metal surface to the introduction of an impurity, considering the Cu(1 1 1) surface as an example. We show that taking explicitly into account the realistic Cu(1 1 1) surface band structure, which is characterized by the energy gap at the center of surface Brillouin zone (SBZ) and the s–p$_z$ partly occupied surface state, is crucial for the description of the surface response.

In order to evaluate the ICD, we adopt an approach based on linear response theory in which an external perturbation $V_{\text{ext}}(\mathbf{r}';\omega)$ and the corresponding ICD $n_{\text{ind}}(\mathbf{r};\omega)$ are related by the equation

$$n_{\text{ind}}(\mathbf{r};\omega) = \int \mathrm{d}\mathbf{r}'\chi(\mathbf{r},\mathbf{r}';\omega)V_{\text{ext}}(\mathbf{r}';\omega). \tag{1}$$

Here $\chi(\mathbf{r},\mathbf{r}';\omega)$ is the density-response function which is non-local and complex and contains information on electronic excitations. In time-dependent density functional theory $\chi(\mathbf{r},\mathbf{r}';\omega)$ satisfies the integral equation [22]

$$\chi = \chi^0 + \chi^0(v_{\text{c}} + K_{\text{xc}})\chi \tag{2}$$

with $\chi^0(\mathbf{r},\mathbf{r}';\omega)$ being the response function of a non-interacting electron system, $v_{\text{c}}(\mathbf{r}-\mathbf{r}')$ is the Coulomb potential, and $K_{\text{xc}}(\mathbf{r},\mathbf{r}';\omega)$ accounts for dynamical exchange-correlation effects. As we are mainly interested in the evaluation of long-range charge-density oscillations, we use the random phase approximation, i.e., $K_{\text{xc}} = 0$. The inclusion of a non-zero K_{xc} mainly affects the amplitude of Friedel oscillations [23–25].

To describe the Cu(1 1 1) surface, we employ a slab containing 81 atomic layers of Cu together with a vacuum region corresponding to 20 interlayer spacings. The substrate is described by a model one-dimensional potential of Ref. [26]. This potential reproduces the key ingredients of the Cu(1 1 1) electronic structure shown in Fig. 1(a), namely, the energy gap at the center of the SBZ and the s–p$_z$ surface and image-potential states in it. Using translation invariance parallel to the surface, one can perform the 2D Fourier transform for all quantities in Eq. (1). The ICD has now the following form [23]:

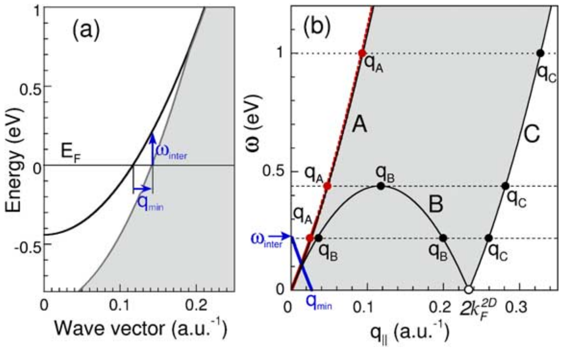

Fig. 1. (a) Surface electronic structure of Cu(1 1 1). The grey area represents the projected bulk electronic structure. Solid line shows the surface state dispersion with an effective mass of $m^* = 0.42m_{\text{e}}$. (b) The phase space available for e–h excitations. In the grey area the surface state intraband e–h excitations are permitted. The intraband e–h bulk excitations are possible everywhere. The interband "surface state–bulk" transitions are forbidden in the area below the blue line. Lines A, B, and C are, respectively, described by equations $\omega = v_{\text{F}}^{\text{2D}}q_{\|} + q_{\|}^2/2m^*$, $\omega = v_{\text{F}}^{\text{2D}}q_{\|} - q_{\|}^2/2m^*$, and $\omega = -v_{\text{F}}^{\text{2D}}q_{\|} + q_{\|}^2/2m^*$ with v_{F}^{2D} being the 2D (surface state) Fermi velocity. Red line shows the acoustic surface plasmon (ASP) dispersion [27] very close to the line A (solid red line corresponds to the well defined ASP, whereas dashed one indicates the region of its gradual degradation). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)