Long-Range Electron-Phonon Coupling at Metal Surfaces

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Long-range scattering of slow electrons by phonon excitations at flat and clean Cu(100) and Ni(100) surfaces has been observed in high-resolution electron-energy-loss measurements. We show that the strength of this electron-phonon coupling derives from the oscillatory response of the electrons at the metal surface. We have evaluated the electron-scattering cross section within the jellium model for the electron response and find excellent agreement with the experimental results.

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The interaction between an external probe of electrons or photons and the electrons and ions in the surface region of a metal is a central problem in a number of surface spectroscopies. In this Letter we present evidence from high-resolution electron-energy-loss measurements for dipole excitation of phonons at metal surfaces by low-energy electrons. We have analyzed these observations quantitatively using a jellium calculation and obtain very good agreement with the experimental results. Schaich and Schwartz[1] have recently discussed this problem using a hydrodynamic description of the electron and ion motion. They notice that the appropriate boundary conditions are not obvious when using such a phenomenological model. Our analysis relies on an observation first discussed by Budd and Vannimenus.[2] The *total force* which acts on the ion cores from the incident electron is *zero,* within the assumption of linear response. This implies that the screened potential induced by an external electron must exhibit oscillations, which is also confirmed by explicit calculations for a semi-infinite jellium.[3] We have used these calculations to estimate the force on the ion cores. We find that the electron-phonon coupling contributes significantly to the surface response function, $g(q_{\parallel},\omega)$, below the maximum energy of the longitudinal bulk phonons.

We will concentrate our discussion on electron-energy-loss spectra (EELS) for the clean Cu(100) surface but will also present some results for Ni(100). Following standard procedures the specimens were cleaned initially by argon-ion bombardment and annealing, and between successive measurements by a brief heating to 950 K [Cu(100)] and 1100 K [Ni(100)], and cooled to measurement temperature at an ambient pressure in the 10^{-11}-Torr range. The surface structure was monitored by low-energy electron diffraction (LEED). The EELS measurements reported in this work were obtained with use of a high-resolution spectrometer of cylindrical mirror construction that has been described elsewhere.[4] The scattering plane containing the incident and collected electron beams is defined by the specimen surface normal and the [100] direction in the surface plane. The polar angles of incidence and collection can be varied independently by rotating the specimen and the analyzer, respectively. The electron energies quoted in the spectra are referred to the vacuum level.

Figure 1 shows the low-energy region of the inelastic electron scattering spectra from the clean Cu(100) and Ni(100) surfaces. The spectra were measured in the specular direction and display both the energy-gain and -loss regions. The characteris-

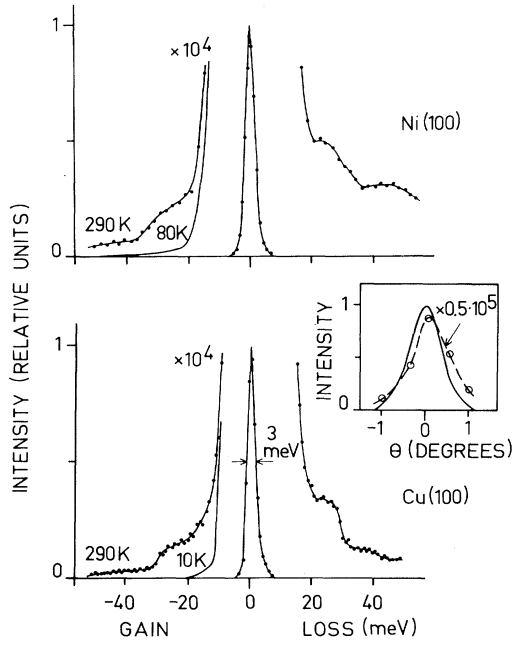

FIG. 1. Electron-energy gain and loss spectra from the Cu(100) and Ni(100) surfaces measured in the specular direction, $\theta = 0°$, for a 2.3-eV electron beam incident at 55°. The loss regions of the spectra show a smooth general decrease of inelastic intensity at the low temperatures, but an accurate measurement is more difficult than for the gain region. The inset shows the elastic peak intensity (solid curve) and the inelastic intensity at 25-meV loss energy (open circles) for Cu(100) vs collection angle θ (positive towards the surface normal).

tic feature of these spectra is an abrupt increase in the inelastic background at ~ 30 meV for Cu(100) and ~ 36 meV for Ni(100) These energies are just identical to the maximum longitudinal phonon energies along the [100] direction for Cu and Ni, respectively.[5,6] The intensity in the gain region is strongly reduced in the low-temperature spectra, obtained at 10 K for Cu and 80 K for Ni. The spectral shape, at 10 K for Cu, is essentially that of the elastic peak as determined by the electron spectrometer. We can accordingly subtract the contribution of the elastic peak from the spectrum measured at 290 K and then determine the shape of the inelastic energy distribution. For gain (at 290 K) and loss energies larger than the maximum phonon energies there is still a significant level of inelastic scattering. This derives from electron-hole pair excitations and these processes evidently add to the inelastic intensity below the maximum phonon energy. This contribution is well understood and we can estimate its intensity as shown below and hence in detail analyze the phonon contribution.

The inset in Fig. 1 shows the angular distributions of elastically and inelastically scattered electrons for Cu(100) at 290 K using 2.3-eV incident electrons. The inelastic intensity is measured at 25 meV, i.e., just below the phonon-loss threshold after subtracting a smoothly extrapolated background. The elastic intensity distribution (solid curve) is symmetrical around the specular direction and has a full width at half maximum of 0.90°. The inelastic distribution is sharply peaked in the specular direction which is characteristic for dipole excited transitions. The electron-phonon scattering evidently takes place via this long-range scattering mechanism.

The experimental results discussed above show that the long-range dipole interaction dominates the inelastic electron-scattering process. Hence the probability $P(\vec{k},\vec{k}')d\Omega_{k'}d\hbar\omega$ that an incident electron of wave vector $\vec{k}$ is scattered inelastically into the solid angle $d\Omega_{k'}$ around the direction of $\vec{k}'$ (the wave vector of the scattered electron) losing energy in the range $\hbar\omega$ and $\hbar(\omega+d\omega)$ is given by[7]

$$P=\frac{2}{(ea_0\pi)^2}\frac{1}{\cos\alpha}\frac{k'}{k}\frac{q_{\parallel}}{(q_{\parallel}^2+q_{\perp}^2)^2}\times(n_\omega+1)\mathrm{Im}g(q_{\parallel},\omega), \quad (1)$$

valid for small momentum transfer, $q_{\parallel} \ll k$. Here α is the angle of incidence, $\hbar\vec{q}_{\parallel}=\hbar(\vec{k}_{\parallel}-\vec{k}'_{\parallel})$ and $\hbar q_{\perp}=\hbar(k_{\perp}-k'_{\perp})$ are the changes in the parallel and normal components of momentum, respectively, $a_0\simeq 0.53$ Å is the Bohr radius, and $n_\omega=[\exp(\hbar\omega/k_BT)-1]^{-1}$ is the Bose-Einstein factor. Equation (1) gives the scattering probability on the loss side; on the gain side $(n_\omega+1)$ must be replaced by $n_{|\omega|}$. The formal definition of the linear-response function $g(q_{\parallel},\omega)$ is given by Persson[8]—here we will need[9] the relation between Img and the power absorption in the metal, $\hbar\omega w$, caused by an evanescent external electric potential

$$\Phi_{\mathrm{ext}}=\Phi_0[\exp(-q_{\parallel}z+i\vec{q}_{\parallel}\cdot\vec{x}_{\parallel}-i\omega t)+\mathrm{c.c.}]$$

($z>0$ in the metal):

$$\mathrm{Im}g=\pi\hbar w/(Aq_{\parallel}|\Phi_0|^2), \quad (2)$$

where A is the surface area. The energy absorption in the metal is due to excitation of electron-hole pairs and phonons so that in general

$$\mathrm{Im}g=(\mathrm{Im}g)_{\text{e-h pair}}+(\mathrm{Im}g)_{\text{phonon}}. \quad (3)$$

The contribution to Img from e-h pair excitations has been discussed earlier[10] and here we will mainly focus on the phonon contribution. Our discussion

will be based on the following observation. The total force which acts on the metal ion cores from the incident electron is zero, within the assumption of linear response. This result, first discussed by Budd and Vannimenus[2] implies that we have a force sum rule $\sum \vec{F}_i = 0$ where $\vec{F}_i$ are the forces which act on the individual ion cores.

From the force sum rule it follows that the screened potential induced by an external electron *must* exhibit oscillations or be identically zero. Simple models, such as the hydrodynamic model where the screened potential decays monotonically towards zero into the "metal," violate the force sum rule. On the other hand, the calculation by Lang and Kohn[3] of the screened potential for a semi-infinite jellium satisfies the force sum rule[11] and we will make use of this calculation below to estimate the force on the ion cores.

Figure 2 shows the z variation of the screened electric field E as calculated by Lang and Kohn[3] for $\omega = 0$, $q_{\parallel} = 0$, and $r_s = 3$. The monovalent ion-core layers are represented by slabs of uniform positive background along the z axis as depicted in the figure. The amplitude of the Friedel oscillations decays rather rapidly with increasing z [$E_z \sim z^{-2} \times \cos(2k_F z + \gamma)$ as $z \rightarrow \infty$] and in the simplest possible model one therefore assumes that the screened electric field is nonzero only at the two topmost layers of ions. To satisfy the force sum rule, opposite forces of identical magnitudes, F and $-F$, must then act on the two layers of ions. Within linear response theory, these forces are linearly related to the electric field E_0 just outside the metal, i.e., $F = \lambda |e| E_0 \equiv e^* E_0$ where $|\lambda| < 1$ is a screening parameter and $|e|$ the charge of the ion. We have defined an effective charge $e^* = \lambda |e|$.

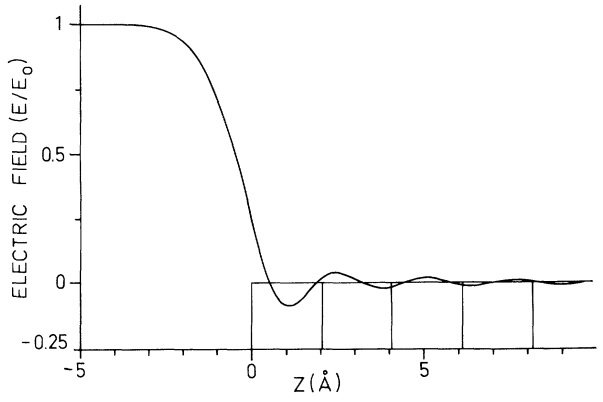

FIG. 2. Variation normal to the surface of the screened electric field, $E(z)$, calculated (Ref. 3) for $\omega = 0$, $q_{\parallel} = 0$, and $r_s = 3$. The division of the uniform positive background into slabs corresponding to monovalent ion-core layers in the [100] direction of a fcc crystal is depicted.

For dipole scattering and low-energy excitations, the momentum transfer $\hbar q_{\parallel}$ is very small: $q_{\parallel} \sim k\hbar\omega/2\epsilon_0 \sim 0.01$ Å^{-1} when $\hbar\omega \sim 10$ meV and $\epsilon_0 \sim 1$ eV. Thus only bulk phonons which propagate normal or almost normal to the metal surface can be excited. These phonons correspond to rigid displacements of the lattice planes against each other. Thus we have a simple one-dimensional problem for the phonon dynamics:

$$\begin{aligned} &M\ddot{u}_0 + M\Omega^2(u_0 - u_1) = e^* E_0, \\ &M\ddot{u}_1 + M\Omega^2(2u_1 - u_0 - u_2) = -e^* E_0, \\ &M\ddot{u}_i + M\Omega^2(2u_i - u_{i-1} - u_{i+1}) = 0, \\ &\qquad\qquad i = 2, 3, \ldots, \end{aligned} \tag{4}$$

Here u_i is the displacement from the equilibrium position of an ion (mass M) in the i th lattice plane and Ω^2 is determined by the force constant between the lattice planes. This system of equations is easily solved for the dipole moment $p = e^*(u_0 - u_1)$ and hence polarizability $\alpha \equiv p/E_0$:

$$\alpha(\omega) = (4e^{*2}/M\omega_0^2) f(\omega), \tag{5}$$

where

$$f(\omega) = 1 + 4\bar{\omega}^2 - 8\bar{\omega}^4 + i8\bar{\omega}^3(1 - \bar{\omega}^2)^{1/2}. \tag{6}$$

We have introduced $\bar{\omega} = \omega/\omega_0$ where $\omega_0 = 2\Omega$ is the maximum longitudinal phonon frequency in the [100] direction. Since there are $2A/a^2$ ions (a = lattice constant = 3.61 Å for Cu) on the surface area A, the total, time averaged (denoted by $\langle\ \rangle$), power absorption is

$$\begin{aligned} \hbar\omega w &= (2A/a^2)\langle \dot{p} E_0 \rangle \\ &= 16(A/a^2)\omega q_{\parallel}^2 |\Phi_0|^2 \mathrm{Im}\alpha(\omega). \end{aligned}$$

Substituting this into (2) gives

$$(\mathrm{Im}g)_{\mathrm{phonon}} = 4q_{\parallel} a (e^*/e)^2 (\omega_{\mathrm{ion}}/\omega_0)^2 \mathrm{Im} f(\omega), \tag{7}$$

where $\omega_{\mathrm{ion}} = [4\pi e^2/(Ma^3/4)]^{1/2}$ is the unscreened ion-plasma frequency. For copper we have[5] $\hbar\omega_0 = 30$ meV and $\hbar\omega_{\mathrm{ion}} = 32$ meV.

In EELS one does not measure $P(\vec{k}, \vec{k}')$ directly, but rather P integrated over the angle of detection $\Delta\Omega$:

$$\Delta P = \int_{\Delta\Omega} P d\Omega.$$

The black dots in Fig. 3 show the experimental

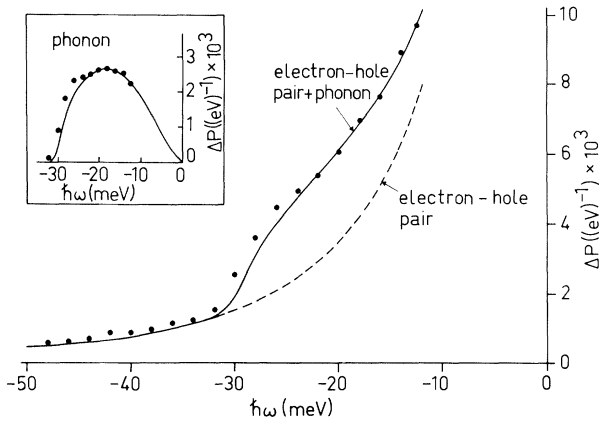

FIG. 3. The filled circles show the experimental gain probability, ΔP, for Cu(100) at 290 K. The dashed and solid curves show the calculated contributions to ΔP from electron-hole pair excitations and the sum of electron-hole pair and phonon excitations, respectively. The inset show separately the experimental (filled circles) and calculated (solid curve) phonon contribution to ΔP.

Cu(100) room-temperature data for $\Delta P(\hbar\omega)$ on the gain side as obtained from Fig. 1 by subtracting the elastic tail (given by the 10-K measurement) from the room-temperature data. The dashed line is the theoretically calculated contribution to $\Delta P(\hbar\omega)$ from electron-hole pair excitations using the theory described in Refs. 8 and 10. The full line is the result obtained after adding the phonon contribution calculated from Eqs. (1), (3), and (7). In this calculation we have used $e^* = 0.0155e$ which is the only adjustable parameter in the theory. The agreement between theory and experiment is excellent. The solid line in the inset shows the phonon contribution separately which also agrees very well with the experimental data (black dots).

The screening parameter $\lambda = e^*/e \simeq 0.016$ shows that the force on the lattice ions in the first layer is reduced to 1.5% of its unscreened value. This result agrees well with the prediction of the jellium calculation (Fig. 2) from which an estimate of λ can be obtained by averaging $E(z)/E_0$ over a layer of ion cores, taken as a slab of positive background, centered at an ion nucleus, and of thickness given by the interplane separation in the [100] direction of a fcc crystal. For $r_3 = 3$ this gives $\lambda_1 = -0.011$, $\lambda_2 = 0.008$, $\lambda_3 = 0.005$, $\lambda_4 = -0.0003$, $\lambda_5 = -0.002$, $\lambda_6 = -0.0002, \ldots$, which should be compared with our result $\lambda_1 = -0.016$, $\lambda_2 = 0.016$, $\lambda_3 = \lambda_4 = \ldots = 0$.[12] The agreement between the result of the jellium calculation and the experiment is even more striking if one accounts for the extended nature of the Friedel oscillations by using a more detailed model for the phonon dynamics. We then find that the calculated electron-scattering cross section for Cu (interpolation to $r_s = 2.7$) is only 10% larger than the experimental value.

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[11]In the jellium model the condition is that $\int_0^\infty dz\, E(z) = \Phi(0) = 0$. I.e., the induced electrostatic potential should be zero at the jellium edge.

[12]Cu is monovalent and has $r_s = 2.7$. The values for λ_i for this r_s are about 20% smaller on the average than for $r_s = 3$.