Long-Range Scattering of Electrons by Electron-Hole Pair Excitations at Metal Surfaces

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The low-energy regime (0.1–0.3 eV) of the electron-energy-loss spectrum from a clean Cu(100) surface has been measured. The experimental data show excellent agreement with predictions from a jellium calculation of the response function $g(q_{\parallel},\omega)$. The weak inelastic signal derives from long-range excitation of electron-hole pairs; the surface potential and the spatial variation of the potential from the probing electron are the prime momentum sources.

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It has recently been suggested[1] that electron-energy-loss spectroscopy (EELS) should provide a useful probe of the surface response function $g(q_{\parallel}, \omega)$. This quantity, which is the surface analog of the bulk dielectric function $\epsilon(\vec{k}, \omega)$, determines the influence of a metal surface on all dynamical processes occurring outside of it. The recent review work by Feibelman[2] contains a number of illustrative applications of $g(q_{\parallel}, \omega)$ to problems like, e.g., the surface photoelectric effect, the surface power absorption, and the friction force on a charged particle. Other examples are the van der Waals interaction between an atom and a metal[3] and the nonradiative damping of an excited atom outside a metal surface.[4] The purpose of this Letter is to present experimental evidence which shows that the low-energy regime of the electron-energy-loss spectrum from a metal surface is determined by $g(q_{\parallel}, \omega)$. The experimental data reveal that the predominant contribution to the inelastic scattering probability comes from the long-ranged Coulomb coupling between the electron and the metal surface. The implications of the experiment are sorted out via a comparison with predictions from a theoretical calculation of $g(q_{\parallel}, \omega)$ for jellium,[5] which shows that, in the zero-temperature limit, the probability for electron-hole pair excitations is governed by both the surface potential and the spatial variation of the potential from the incident electron.

The electron-energy-loss measurements reported in this work were obtained from the clean Cu(100) surface. At the low excitation energies investigated, 0.1–0.3 eV, copper can be considered as a reasonably simple metal. It is also fairly inert which facilitates the measurements of the weak inelastic signal from the clean metal surface. The specimen was cleaned routinely by argon-ion bombardment and annealing. Between successive measurements the crystal was cleaned by a brief heating to 950 K 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 EEL spectra were recorded with use of a high-resolution electron spectrometer of cylindrical-mirror construction, which has been described briefly elsewhere.[6] The specimen and the analyzer can be rotated such that the polar angles of incidence and collection can be varied independently. The scattering plane containing the incident and the collected electron beams is defined by the specimen surface normal and the [100] direction in the surface plane. The work-function difference between the spectrometer and the specimen was compensated to within better than 0.05 eV and the electron energies quoted refer to the vacuum level. The experimental data (shown in Figs. 1–3) were obtained for an angle of incidence $\alpha = 54°$ (relative to the surface normal) and a spectrometer energy resolution of 4.5 meV. Except for the specific angular measurements all energy-loss spectra were measured in the specular direction.

The experimental results discussed below show that the long-range dipole interaction is the predominant mechanism contributing to the inelastic electron scattering process. Hence the probability $P(\vec{k}, \vec{k}')d\Omega\hbar\, d\omega$ that an incident electron, of wave vector $\vec{k}$, is scattered inelastically into the solid angle $d\Omega$ around the direction of $\vec{k}'$ (the wave vector of the scattered electron) losing en-

ergy in the range $\hbar\omega$ and $\hbar(\omega+d\omega)$ is given by standard dipole scattering theory[7]:

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

valid for small momentum transfer, $q_\parallel \ll k$. Here α is the angle of incidence, and $\hbar\vec{q}_\parallel=\hbar(\vec{k}_\parallel-\vec{k}_\parallel')$ and $\hbar q_\perp=\hbar(k_\perp-k_\perp')$ are the changes in the parallel and normal components of momentum, respectively. The experimentally measured inelastic scattering probability, ΔP, relates simply to P integrated over the solid angle of detection $\Delta\Omega$,

$$\Delta P=\int_{\Delta\Omega}P\,d\Omega. \quad (2)$$

In general, all the elementary excitations of the metal such as electron-hole pairs, phonons, and magnons will contribute to Img. Here we will consider excitation energies $\hbar\omega$ well above the highest phonon frequency of the metal and only electron-hole pairs contribute significantly. The excitation of the metal electrons requires conservation of energy as well as momentum. One can distinguish between three sources of the required momentum: (a) From the bulk, the momentum needed can come either from intraband transitions aided by phonons or impurities or from the crystal potential, i.e., interband transitions. Momentum can also come (b) from the surface potential and (c) from the spatial variations of the potential from the perturbing charges, i.e., in this case the incident electron. The contributions from (a) and (b) were treated in Ref. 1 and given as follows:

$$(\mathrm{Im}g)_a=\mathrm{Im}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\approx\frac{\omega}{\omega_p}\frac{1}{k_Fl}\left(4\frac{\omega_F}{\omega_p}\right), \quad (3)$$

where the last equality is valid if $\epsilon(\omega)$ is well approximated with a Drude dielectric function, i.e., $\epsilon(\omega)\approx1-\omega_p^2/\omega(\omega+i/\tau)$ and $1/\tau,\ \omega\ll\omega_p$; ω_p is the plasma frequency of the metal, k_F is the electron Fermi wave vector, and l is the electron mean free path.

$$(\mathrm{Im}g)_b=2\xi(r_s)(q_\parallel/k_F)\omega/\omega_p, \quad (4)$$

derived within a jellium description of the metal and valid for $q_\parallel\ll k_F$ and $\omega\ll\omega_p$. The parameter $\xi(r_s)$ depends on the electron-gas density parameter r_s. During the course of these experiments it was concluded that the contribution from process (c) was substantial. The following expression has been derived[5] for (c) valid for the same situation as (b), i.e., a jellium description of the metal, $q_\parallel\ll k_F$ and $\omega\ll\omega_p$:

$$(\mathrm{Im}g)_c=(\omega/\omega_p)^2\eta^3G(\eta), \quad (5)$$

where $\eta=\omega k_F/2\omega_F q_\parallel$ and

$$G(\eta)=\begin{cases}8 & \text{for } \eta<1,\\ 8[1-(1+\frac{1}{2}\eta^{-2})(1-\eta^{-2})^{1/2}] & \text{for } \eta>1.\end{cases} \quad (6)$$

One should expect processes (a) and (c) to interfere (i.e., they are not just additive) but we will particularly focus on the zero-temperature limit where the Drude contribution to Img vanishes. Thus, if we neglect the interference between processes (a) and (c), Eqs. (3)–(5) give the final result

$$\mathrm{Im}g=\frac{\omega}{\omega_p}\left(\frac{a}{k_Fl}+b\frac{q_\parallel}{k_F}+\frac{\omega}{\omega_p}\eta^3G(\eta)\right), \quad (7)$$

where $a=4\omega_F/\omega_p$ and $b=2\xi$. Treating copper as a free-electron metal with $r_s=2.67$ corresponding to one free electron per copper atom gives $a\approx2.6$ and $b\approx1.13$.

The angular distributions for elastically and inelastically (0.1- and 0.3-eV energy loss) scattered electrons measured for 2.3-eV incident electrons and a specimen temperature of 293 K are shown in Fig. 1. A narrow energy window of ±25 meV around the specific loss energy was recorded and inspected for any contribution from discrete vibrational excitations related to surface contamination. The elastic intensity distribution (solid curve) is symmetrical around the specular direction, $\theta=0$, and has a full width at half maximum of 0.90°. The two inelastic intensity distributions show broader peaks with maxima cen-

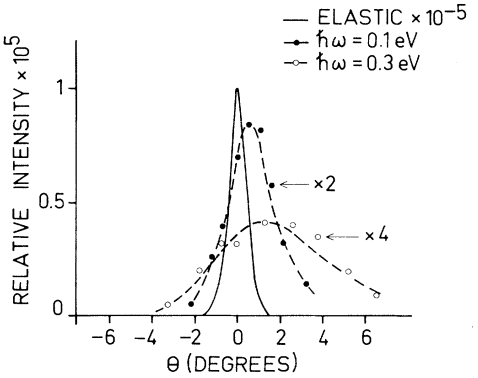

FIG. 1. Experimental elastic and inelastic ($\hbar\omega$ = 0.1 and 0.3 eV) intensity vs collection angle θ (θ = 0 specular, $\theta>0$ towards surface normal) scattered from Cu(100) at 293 K. Energy of incident electron beam, 2.3 eV; and angle of incidence, 54°.

tered close to the specular direction; the widths relate approximately as the corresponding loss energies. These are characteristic features for dipole excited transitions[6] and the inelastic electron scattering apparently takes place via the long-range–dipole interaction.

Figure 2 shows how the inelastic scattering probability, ΔP [see Eq. (2)], depends on the loss energy $\hbar\omega$. The inset shows the measured data for ΔP at $\hbar\omega = 0.1$, 0.15, 0.2, and 0.3 eV and for several temperatures. The data were obtained at discrete loss energies, in the way described above, in order to minimize the measurement time between successive cleanings. One notes that for $\hbar\omega = 0.1$ eV, ΔP varies linearly with temperature which is also expected from optical data for Cu.[8] This is also the prediction from the standard theory[9] of phonon resistivity for $T > 0.2T_D$ (where T_D is the Debye temperature). The open circles in Fig. 2 correspond to the ΔP values obtained by extrapolating the data in the inset to $T = 0$. The filled circles show the Drude contribution to ΔP at room temperature as given by $\Delta P(T = 293\ \mathrm{K}) - \Delta P(T = 0\ \mathrm{K})$. The solid curves are theoretically predicted results for ΔP for processes (a) [see Eq. (3)] using $l = 147$ Å and processes (b) + (c) [see Eqs. (4)–(6)]. The agreement between experiment and theory is excellent with respect to the dependence of ΔP on $\hbar\omega$. The mean free path $l = 147$ Å compares favorably with the value 125 Å deduced from optical data for Cu.[8] The absolute value of ΔP deviates only by 35% from the theoretical result and as will be seen below on the average by less than 20% over a range of impact energies. The dependence of ΔP on the incident electron energy is shown in Fig. 3. The open and filled circles correspond to the experimental data for $\hbar\omega = 0.1$ eV obtained at 293- and 80-K substrate temperature, respectively. The solid curves correspond to the calculated contributions from processes (a) + (b) + (c), (b) + (c), and (b), respectively. The Drude contribution, process (a), at $T = 293$ K was calculated for the mean free path $l = 147$ Å found above. The agreement between experiment and theory [the $T = 293$-K data (open circles) should be compared with (a) + (b) + (c)] is very good, as regards the dependence of ΔP on the incident electron energy, the absolute value of ΔP, and the relative magnitude of the Drude contribution. The importance of the contribution (c) is obvious from Fig. 3. The agreement between the experimental data for a copper surface and the predicted theoretical results for a jellium surface is in fact surprisingly good. Copper is not a perfect free-electron-like metal; for example, both the work function [which affects process (b)] and the effective electron mass [which affects processes (b) and (c)] differ from the prediction of the jellium model and this must be accounted for in a more accurate calculation.

In conclusion, it is noted that the low-energy

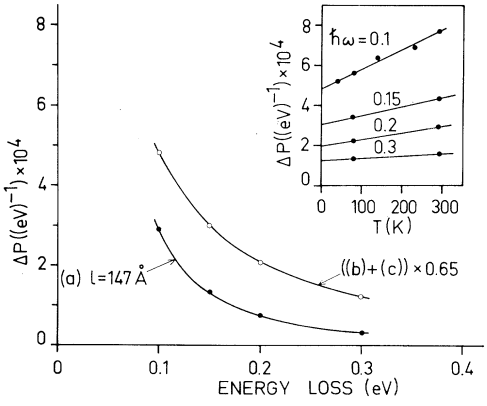

FIG. 2. Inelastic scattering probability ΔP vs loss energy, $\hbar\omega$, and temperature, T (see inset), for 2.3-eV electrons; specular condition. The open and filled circles represent the extrapolated experimental $\Delta P(T = 0\ \mathrm{K})$ and $\Delta P(T = 293\ \mathrm{K}) - \Delta P(T = 0\ \mathrm{K})$ data, respectively. The solid curves are the theoretically predicted results for processes (a) and (b) + (c), respectively (see text).

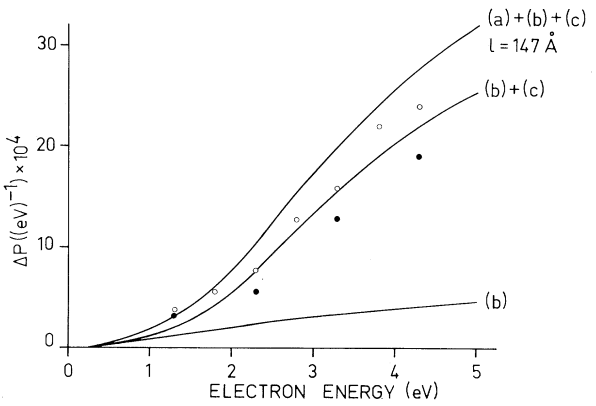

FIG. 3. Inelastic scattering probability ΔP vs incident electron energy. The open and filled circles denote the experimental ΔP values at $T = 293$ K and $T = 80$ K, respectively, for 0.1-eV loss energy and specular condition. The solid curves are the calculated results for processes (b), (b) + (c), and (a) + (b) + (c), respectively (see text).

regime of the electron-energy-loss spectrum from a clean Cu(100) surface shows remarkably good agreement with predictions from a theoretical calculation of the linear response function $g(q_{\parallel},\omega)$ for a jellium surface. This is an interesting result of substantial general importance since $g(q_{\parallel},\omega)$ is such a central quantity in the description of dynamical processes outside a metal surface.

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