

Surface-Plasmon Dispersion in Simple Metals

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Angle-resolved reflection inelastic electron scattering has been used to measure the dispersion of the surface plasmon for thick films of Na and K. The measured dispersion is negative at small momentum parallel to the surface as predicted by quantum-mechanical calculations of the dynamic response of the electrons at the surface of an interacting electron gas. A simple physical picture is presented to explain the origin of the negative surface-plasmon dispersion in simple metals.

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Dynamical screening effects are at the heart of many important surface processes, notably energy transfer between incident particles and substrates, reflection of light, etc. Theory has shown that in the long-wavelength limit all such effects can be described by two surface response functions, $d_{\perp}(\omega)$ and $d_{\parallel}(\omega)$, which embody the position and power spectrum of a surface with respect to the normal and parallel electric fields, respectively.¹ As long ago as 1973, the theoretical result for $\text{Re}d(\omega)$ was understood to predict a very unusual result, namely that the long-wavelength surface plasmon (ω_{sp}) should manifest a negative dispersion, i.e., $d\omega_{\text{sp}}/dq_{\parallel}|_{q_{\parallel} \rightarrow 0} < 0$.² We present here a definitive experimental verification of this prediction, and discuss its significance.

The first prediction of a surface plasmon came from Ritchie³ in 1957, followed by Stern and Ferrell⁴ in 1960 using a macroscopic dielectric treatment. The requirement that the normal component of the displacement vector be continuous in passing across the interface gives the criterion for a surface plasmon, i.e., $\epsilon(\omega_{\text{sp}}) = -1$, or for simple metals that $\omega_{\text{sp}} = \omega_p/\sqrt{2}$, where ω_p is the bulk plasmon given by $(4\pi ne^2/m)^{1/2}$ (n is the electron density). Powell and Swan verified the existence of surface plasmons on surfaces of Al and Mg using reflection electron scattering.⁵

Using a microscopic calculation of the dynamic response of the electrons at the surface of a "jellium solid" Harris and Griffin,⁶ Flores and Garcia-Moniner,⁷ and Feibelman² all derived an expression for the dispersion of the surface-plasmon mode for small wave vector q_{\parallel} (nonretarded limit). Using Feibelman's $d(\omega)$ response functions the surface-plasmon energy $\omega(q_{\parallel})$ can be expressed as

$$\omega(q_{\parallel}) = \omega_{\text{sp}} \{ 1 - q_{\parallel} [d_{\perp}(\omega_{\text{sp}}) - d_{\parallel}(\omega_{\text{sp}})]/2 + \dots \}. \quad (1)$$

The quantity $d_{\parallel}(\omega)$ is the position of the positive background edge, which can be set to zero without loss of generality. With this convention $d(\omega) = d_{\perp}(\omega)$ is the centroid of the charge distribution, $\delta n(z, \omega)$, induced by a weak external field oscillating at frequency ω ,

$$d(\omega) = \int dz z \delta n(z, \omega) / \int dz \delta n(z, \omega). \quad (2)$$

This theoretical treatment of the response of a jellium surface has produced several important predictions about the properties of surface plasmons. (1) ω_{sp} in Eq. (1) is independent of the charge-density profile at the surface.⁸ Therefore, the energy of the surface plasmon at $q_{\parallel} = 0$ is a property of the bulk. (2) At the frequency of the surface plasmon ω_{sp} the induced screen charge is outside of the metal surface, i.e., $d(\omega_{\text{sp}})$ is positive and the surface-plasmon dispersion is negative.^{1,2} In contrast to ω_{sp} , which is insensitive to the properties of the surface, $d(\omega)$ is very sensitive to the charge-density profile at the surface,^{1,2,9,10} leading to considerable theoretical speculation that the magnitude of the surface-plasmon dispersion could be used to improve our knowledge of the electronic density at a metal surface.⁹ (3) ω_{sp} is real but $d(\omega)$ is complex.^{1,11} The dispersion of the surface plasmon is given by $\text{Re}d(\omega)$, while the $\text{Im}d(\omega)$ gives the width. There is no width to the surface-plasmon excitation at $q_{\parallel} = 0$,² but the width should increase linearly with increasing q_{\parallel} .

Since the first observation of surface plasmons, there have been several measurements of the surface-plasmon dispersion at small q_{\parallel} for simple metals, but the results are ambiguous. Kunz¹² observed a negative dispersion for a Mg film in a high-energy electron-loss experiment in the transmission mode. But Kloos and Raether¹³ did not observe a negative dispersion for a Mg film using the same technique. They attributed the discrepancy to surface contamination. Duke *et al.*¹⁴ fitted inelastic low-energy electron diffraction data to a theoretical model reporting a small negative dispersion for the (100) surface of aluminum but the results for the (111) surface were uncertain. In contrast, the data from Krane and Raether¹⁵ and Kloos and Raether¹³ "exclude a negative slope of the dispersion curve" for an Al film.

The dispersion of the surface plasmon was measured using angle-resolved inelastic electron scattering in the reflection mode. An electron beam of energy E is incident upon a sample at an angle θ_i , with respect to the normal. It is inelastically scattered into the angle θ_s , with an energy $E' = E - \hbar\omega$, where $\hbar\omega$ is the energy of the loss. The momentum transfer parallel to the surface,

q_{\parallel} , is given by

$$\hbar q_{\parallel} = (2m)^{1/2} [\sqrt{E} \sin \theta_i - (E - \hbar \omega)^{1/2} \sin \theta_s].$$

The two curves in Fig. 1 show loss spectra from a thick K film for two different scattering geometries. The energy of the peak in the larger q_{\parallel} spectrum is clearly less than the one near $q_{\parallel} = 0$, showing a negative dispersion. Notice also that the line width increases as q_{\parallel} increases, in agreement with theory. The most important observation is that *the surface-plasmon dispersion at small q_{\parallel} is negative for K (and for Na) as predicted by theory using the best self-consistent charge-density profile for the surface.*² There are two discrepancies between experiment and theory, which may be related to the fact that K is not an ideal jellium. The first is that the value of ω_{sp} [Eq. (1)] deduced from Fig. 2 is 2.74 eV while the anticipated value for the density of K would have been 3.0 eV. The second discrepancy is that the line width is not zero at $q_{\parallel} = 0$ as expected theoretically. We will return to discuss these issues later.

These measurements were made with an electron-loss spectrometer (L-H ELS 22) mounted in an ultrahigh-vacuum chamber operated at a pressure of 5×10^{-11} Torr. The incident energy used was normally 15 eV but several other energies were used to assure that the dispersion did not depend upon the incident energy. The incident angle was varied to measure the dispersion, while the scattering angle was kept fixed at about 60° . The

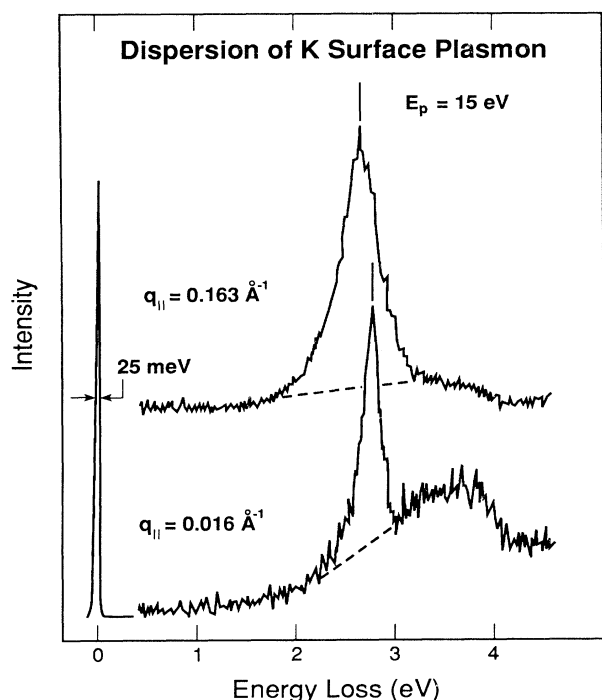


FIG. 1. The inelastic loss spectra from a thick K film grown onto an Al(111) substrate, for two different values of the momentum transfer.

films were prepared by evaporating an alkali metal onto a clean Al(111) surface at 100 K and then annealing to 205 K for K and 240 K for Na. These temperatures were determined by observing the intensity and angular profile of the specularly scattered electron beam for an incident energy of 4 eV. The criteria for the best film were that the reflected intensity be maximized and that the angular profile be narrow. The energy resolution was normally 25 to 35 meV and the angular distribution of the elastic peak was measured to be 2.5° . No LEED pattern was observed, indicating that our films were probably polycrystalline. The film thickness was several hundred angstroms.

Figure 2 is a plot of the measured surface-plasmon dispersion for K over a range of q_{\parallel} from 0 to 0.3 \AA^{-1} . The surface-plasmon energy clearly disperses downward in energy throughout the range of $0 < q_{\parallel} < 0.15 \text{ \AA}^{-1}$ and then upwards rapidly. For large q_{\parallel} , Inglesfield and Wikborg have calculated that the dispersion is not sensi-

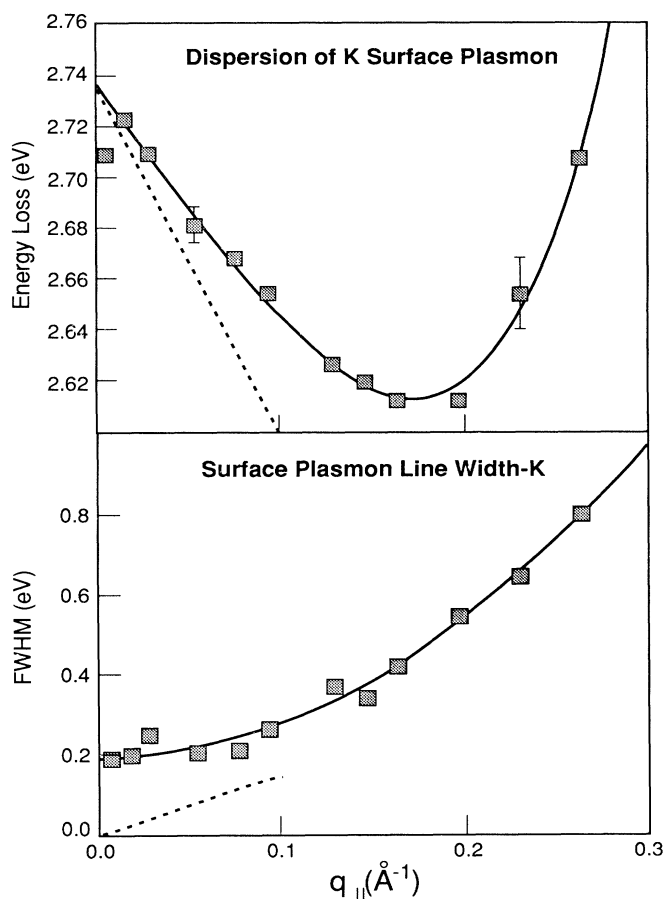


FIG. 2. Top: Measured dispersion of the surface-plasmon energy as a function of q_{\parallel} for a thick K film. The dashed line is Feibelman's prediction for the linear term (Ref. 2). Bottom: Measured line width as a function of q_{\parallel} . The dashed line is the linear slope predicted by Feibelman (Ref. 2). In both cases the measured value of ω_{sp} was used in Eq. (1).

tive to the form of the surface potential and approaches the bulk-plasmon dispersion.¹⁶ The large- q_{\parallel} region of the dispersion curves will not be discussed in this Letter. The experimental data were fitted to a fourth-order polynomial¹⁷ shown by the solid line, and given by

$$\omega(q_{\parallel}) = [2.74 - 1.06q_{\parallel} + 1.54q_{\parallel}^2 - 8.43q_{\parallel}^3 + 62.06q_{\parallel}^4] \text{ eV}.$$

When this is rewritten in the form of Eq. (1) the value of $d(\omega_{sp})$ can be determined,

$$\omega(q_{\parallel}) = 2.74[1 - 0.77q_{\parallel}/2 + \dots] \text{ eV}. \quad (3)$$

Figure 3 displays the data for Na, illustrating that negative dispersion is a general property of the simple metals. The data are again fitted with a fourth-order polynomial over the same range of q_{\parallel} that was used for K in Fig. 2. The best fit is shown by the solid curve and given by

$$\omega(q_{\parallel}) = [3.99 - 1.56q_{\parallel} + 2.47q_{\parallel}^2 - 0.44q_{\parallel}^3 + 47.9q_{\parallel}^4] \text{ eV}.$$

The first-order terms can be written in the form of Eq. (1),

$$\omega(q_{\parallel}) = 3.99[1 - 0.78q_{\parallel}/2 + \dots] \text{ eV}. \quad (4)$$

The dashed lines in Figs. 2 and 3 are the theoretical predictions for the linear term in the surface-plasmon dispersion of K and Na by Feibelman² using a random-phase approximation (RPA) and a Lang-Kohn surface potential. There is really quite remarkable agreement between theory and experiment, especially considering that the theory does not include any band structure in the ground state or any exchange correlation in the dynamics, and the effect of surface roughness on the data is unknown.

A simple physical picture of the relationship between the surface-plasmon dispersion and the associated induced surface charge (or dynamic screening) is present-

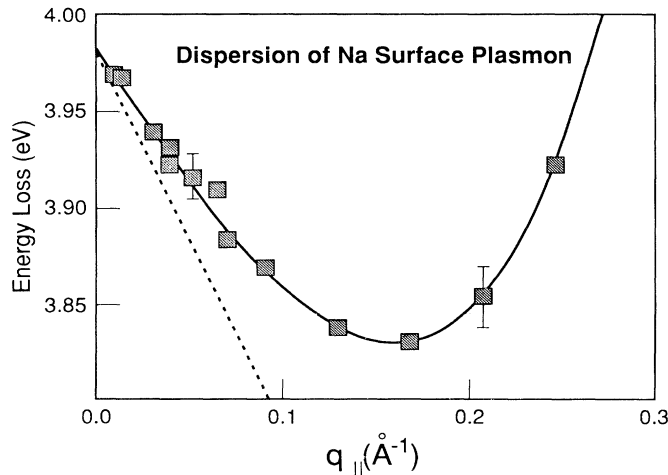


FIG. 3. Surface-plasmon dispersion for a thick Na film as a function of q_{\parallel} . The dashed line is the theoretical prediction (Ref. 2).

ed in Fig. 4.¹⁸ In this figure the induced screening charge $\delta n(z)$ is represented by the dot-dashed curve and ground-state electron distribution $n(z)$ by the dashed line. For simplicity the Friedel oscillations extending into the bulk are not shown. In Fig. 4(a), the induced charge is assumed to be "outside" the metal and in Fig. 4(b) the induced charge is depicted as being "inside" the metal. These two cases represent situations where $d(\omega_{sp})$ is positive and negative, respectively. In the non-retarded region, the electrostatic potential due to the induced charge is given by

$$\phi(z) \approx \int dz' \delta n(z') \exp(-q_{\parallel} |z - z'|)$$

and attenuates like $\exp[-q_{\parallel} |z - d(\omega_{sp})|]$. Each set of curves in Fig. 4 show two potential curves ϕ and ϕ' , where ϕ' is for a larger value of q_{\parallel} . When $d(\omega_{sp})$ is outside the jellium edge (i.e., when d is positive) as shown in Fig. 4(a), as q_{\parallel} increases, less of the metal is subjected to the plasmon's electric field resulting in a lower effective electron density seen by the plasmons field. If $d(\omega_{sp})$ is inside the jellium [Fig. 4(b)], as q_{\parallel} increases, more of the field overlaps the region of high electron density inside the metal and the average electron density responding to the surface-plasmon field increases. It can be proven within RPA that in the long-wavelength limit a surface mode exists at $\omega^2 = (4\pi e^2/m)n_{av}$, where n_{av} is the average unperturbed (ground-state) electron density

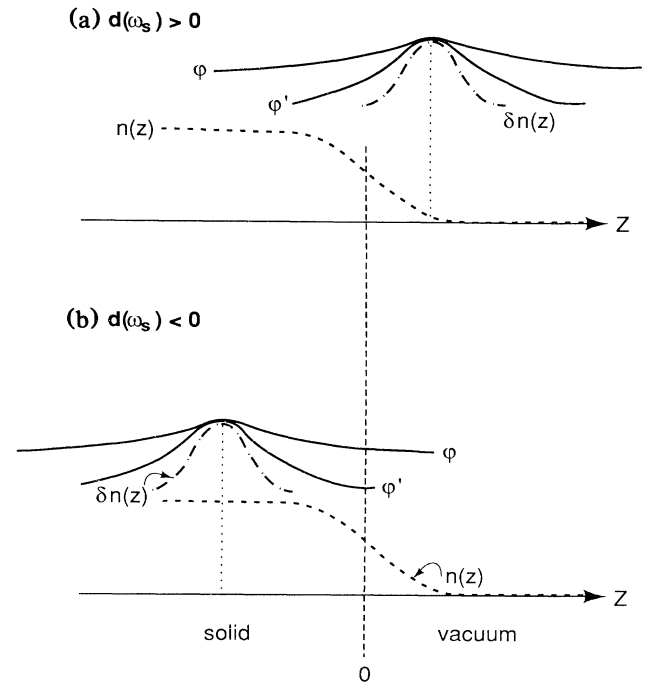


FIG. 4. Illustration of the relation of the position of the induced charge $\delta n(z)$ to the surface-plasmon dispersion. (a) For d outside the jellium edge and (b) for d inside. ϕ' is the electrostatic potential for a larger value of q_{\parallel} than ϕ .

seen by the electrostatic potential created by the induced charge.¹⁹ The average density n_{av} is defined by the following equation:

$$n_{av} = \int dz n(z) \phi(z) / \int dz \phi(z), \quad (5)$$

with the potential $\phi(z)$ given previously in this paragraph and $n(z)$ being the unperturbed electron-density profile. In the small- $q_{||}$ approximation, Eq. (5) reduces to $n_{av} = (n/2)(1 - q_{||}d)$, which gives the same dispersion equation as deduced from more rigorous calculations and given in Eq. (1) (n is the bulk density).

Our data coupled with the simple physical picture presented in Fig. 4 prove that *the induced screening charge at the surface of a simple metal is located outside the metal, in the tail of the charge-density profile*. The centroid position is outside the jellium edge because the electrons spilling out into the vacuum are more compressible than the higher-density electron gas inside the solid.

The introduction to this paper indicated that the measured dispersion of the surface plasmon at small q could be used to test different theoretical models of the charge-density profile at the surface. Before this can be done there are several issues that need to be addressed both experimentally and theoretically. The line width of the K plasmon shown in Fig. 2 indicates that there is some fundamental physics missing in our description of the surface plasmon, since "jellium" theory predicts no width at $q_{||} = 0$ (dashed line). The observed finite width could be a result of the damping due to the band structure of the solid or due to surface roughness.⁹ In either case, the magnitude of the measured dispersion should be a lower limit to the dispersion for an ideal flat jellium solid. Another theoretical concern has to be the validity of RPA¹ to treat the dynamics.

Liebsch has calculated the dynamic response at the surface of jellium using a "time-dependent local-density approximation" which includes a local approximation to exchange and correlation in the dynamical calculation.²⁰ The conclusion from this calculation is that dynamical exchange and correlation has a large effect on the sur-

face-plasmon dispersion for the lower-density metals. There is over a twofold increase in $d(\omega_{sp})$, compared to a RPA calculation, for K. Since there is no unique way of including exchange and correlation in the dynamics, different schemes need to be investigated.

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