

## Surface-Plasmon Energy and Dispersion on Ag Single Crystals

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We report here the measurements of the energy and dispersion of the surface plasmons on Ag single crystals in UHV using angle-resolved electron-energy-loss spectroscopy. The energy of small-momentum surface plasmons depends upon crystal face and, for Ag(110), upon crystal orientation. The differences in the energies of the surface plasmons, which cannot be explained by a jellium model, are discussed in terms of the contributions to the dielectric response from surface states and truncated bulk band states.

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The concept of a collective excitation of the electrons near the surface of a metal was introduced in 1957 by Ritchie,<sup>1</sup> and in analogy with the plasma oscillations in the bulk is called a "surface plasmon." In the thirty years since this paper was published surface plasmons have been observed on a wide range of materials, using both electrons and photons as probes.<sup>2</sup> However, only recently have measurements been reported for the energies and dispersions of surface plasmons on simple alkali metals.<sup>3</sup> The simple metals most closely resemble a confined electron gas, from which the concept of a plasmon originated, and for which detailed theoretical calculations exist.<sup>4</sup> The data for K and Na show remarkable agreement between experiment and theory, confirming the idea that "jellium" is a good model for the alkali metals. There are two important conclusions from the work on simple metals that is relevant to this study on Ag. First, the energy of the surface plasmon at small momentum  $q_{\parallel}$  is independent of the surface charge profile and is given by  $\omega \approx \omega_p/\sqrt{2}$ , where  $\omega_p$  is the bulk plasmon energy.<sup>4</sup> The second conclusion is that the dispersion at small  $q_{\parallel}$  is negative. Our objective was to use single crystals of Ag, which is not a free-electron-like metal, to investigate the effects of the surface and bulk band structure on the properties of the surface plasmon. Recent high-resolution electron-energy-loss measurements on Ag(111) have shown a surface plasmon with no negative dispersion.<sup>5</sup>

We report here measurements of the dispersion of the surface plasmons on Ag(111) and Ag(110) single crystals in UHV using angle-resolved high-resolution electron-energy-loss spectroscopy. We find that at small  $q_{\parallel}$  the surface plasmons on the (111) surface and on the (110) surface (with  $q_{\parallel}$  along [001] and [1 $\bar{1}$ 0]) have appreciably different energies, i.e., 3.69, 3.76, and 3.86 eV, respectively. The energy of the surface plasmon on the (110) surface with  $q_{\parallel}$  along [1 $\bar{1}$ 0] is actually greater than that of the ( $q \approx 0$ ) "bulk plasmons" (3.78 eV).<sup>6</sup> Ag is not a free-electron-like metal since the onset of the interband transition occurs at an energy of 3.87 eV,<sup>7</sup> which is far below the energy of  $\sim 9$  eV expected for the

bulk plasmon in the absence of any interband transitions.<sup>8</sup> In fact, the bulk plasmon corresponds to a coupled mode of the free-electron plasma oscillations with the interband transitions. The energies of the surface plasmons on Ag(111) and Ag(110) lie just below the onset of the interband transitions. It is therefore necessary to go "beyond jellium" to interpret these data and, in particular, to take into account the contributions to the dielectric response from interband and surface-state excitations in the surface region. *The anisotropy of the surface-plasmon dispersion on the Ag(110) surface can in fact only arise from the anisotropy of the contributions from interband and surface-state transitions to the dielectric response in the surface region.*

The inelastic electron-loss spectra were measured with a Leybold-Heraeus ELS-22 Spectrometer with a typical incident energy of 15 eV and a resolution of 20 meV. The angle of the scattered electrons was fixed at  $\theta_s \approx 60^\circ$ . The incident angle  $\theta_i$ , measured from the surface normal, was changed to measure both the specular ( $\theta_i = \theta_s$ ) and off-specular ( $\theta_i \neq \theta_s$ ) spectra. Because of the conservation of the tangential momentum component at the surface, the momentum transfer  $q_{\parallel}$  is uniquely determined by  $\theta_i$ ,  $\theta_s$ , and the incident and scattered electron energies,  $E_i$  and  $E_s$ , as follows:

$$q_{\parallel} = (2mE_i/\hbar)^{1/2} [\sin\theta_i - (1 - \Delta E/E_i)^{1/2} \sin\theta_s],$$

where  $\Delta E = E_i - E_s$  is the electron energy loss and  $m$  is the electron mass. Intensity variations with scattering geometry show that the loss peak is dipole active. The observed energy and the width of the surface-plasmon peaks at fixed  $q_{\parallel}$  were independent of the incident electron energy and the scattering angle. The vacuum in the chamber was in the low- $10^{-11}$ -Torr range and the sample was cooled to 100 K to reduce thermal effects. The Ag(111) and Ag(110) single crystals were cut from the same rod within  $2^\circ$ , polished mechanically with alumina particles, and then polished electrochemically. The sample surfaces were cleaned by several cycles of 1-keV Ar- or Ne-ion sputtering and annealing in the UHV chamber. The quality of the surface was checked by

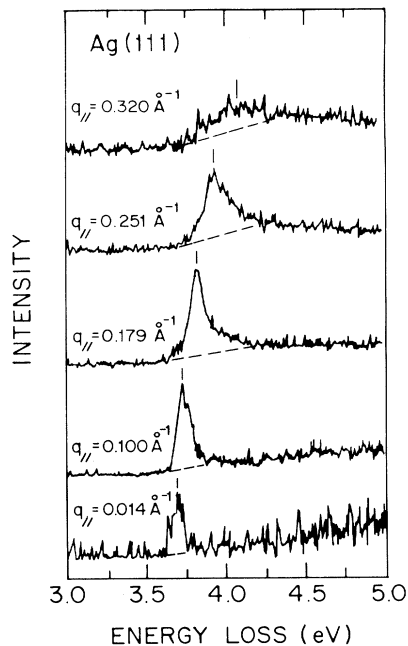


FIG. 1. Electron-energy-loss spectra of the surface plasmon on Ag(111) at 100 K for different values of  $q_{\parallel}$ . The vertical lines indicate the surface-plasmon peak positions.

low-energy-electron diffraction. The measurements were made along the [001] and  $[1\bar{1}0]$  directions on the Ag(110) surface within approximately  $10^\circ$ . The cleanliness of the surfaces was verified by the absence of any loss peaks due to vibration modes of adsorbed molecules on Ag.

Figure 1 shows the electron-energy-loss spectra of the surface plasmons on the Ag(111) surface for increasing values of  $q_{\parallel}$ . The position of the surface-plasmon peak shifts to higher energy with increasing  $q_{\parallel}$ . The deconvoluted widths are quite narrow at small  $q_{\parallel}$  (the width at  $q_{\parallel} \approx 0$  is 63 meV, i.e.,  $\Delta E/E = 0.02$ ), gradually increase with increasing  $q_{\parallel}$ , and then "suddenly" broaden in the region where electron-hole pair excitations occur (Landau damping region).

The energy of the surface-plasmon peaks for Ag(111) and for Ag(110) with  $q_{\parallel}$  along the [001] and  $[1\bar{1}0]$  directions are plotted versus  $q_{\parallel}$  in Fig. 2. Since the spread of the electron beam is  $\pm 1^\circ$ , we cannot observe the effect of retardation at  $q_{\parallel} \approx 0$ . The solid lines are the fitted curves:  $\hbar\omega = 3.69 + 4.17q_{\parallel}^2$  eV for Ag(111),  $\hbar\omega = 3.76 + 3.68q_{\parallel}^2$  eV for Ag(110) in the [001] direction, and  $\hbar\omega = 3.86 + 1.46q_{\parallel}^2$  eV for Ag(110) in the  $[1\bar{1}0]$  direction, where  $q_{\parallel}$  is given in  $\text{\AA}^{-1}$ . Our data for Ag(111) are consistent with the data obtained for that surface at room temperature by Contini and Layet.<sup>5</sup>

The most important result is that the surface-plasmon energy at  $q_{\parallel} \approx 0$  is dependent on the crystal surface and, in the case of Ag(110) surface, on the direction of  $q_{\parallel}$ . A second important observation is that

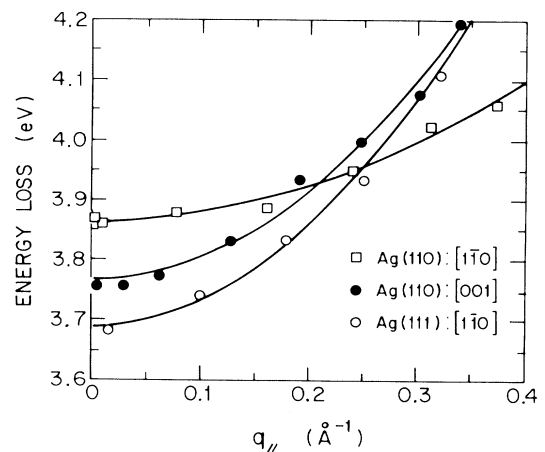


FIG. 2. Dispersion of the surface plasmons on Ag(111) and on Ag(110) with  $q_{\parallel}$  along the [001] ( $=\bar{Y}$ ) and the  $[1\bar{1}0]$  ( $=\bar{X}$ ) directions. The solid lines are fitted quadratic curves as noted in the text.

the energy of the ( $q_{\parallel} \approx 0$ ) surface plasmon on the Ag(110) surface with  $q_{\parallel}$  along  $[1\bar{1}0]$  (3.86 eV) is higher in energy than the ( $q_{\parallel} \approx 0$ ) bulk plasmon of Ag (3.78 eV),<sup>6</sup> a result that is unexpected on the basis of any simple model.

Figure 3 shows the energy-loss spectra at  $q_{\parallel} \approx 0$  for the three different surface orientations. The inherent widths of the surface-plasmon loss peak are 63 meV for Ag(111), 114 meV for Ag(110) with  $q_{\parallel}$  along [001], and 185 meV for  $q_{\parallel}$  along  $[1\bar{1}0]$ . The differences in the

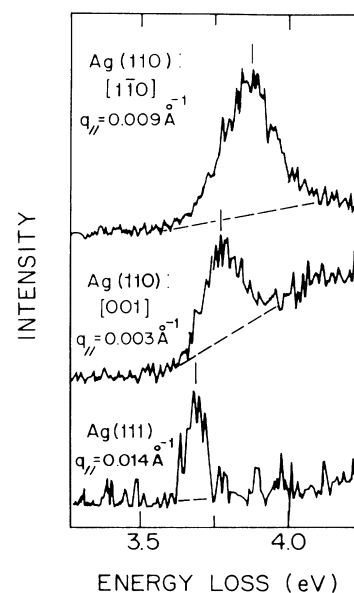


FIG. 3. Electron-energy-loss spectra of the  $q_{\parallel} \approx 0$  surface plasmons on Ag(111) and on Ag(110) with  $q_{\parallel}$  along the [001] and the  $[1\bar{1}0]$  directions.

surface-plasmon energies are larger than their half-widths, and it is easily seen that the width increases with increasing energy. The larger width of the ( $q_{\parallel} \approx 0$ ) surface plasmon on Ag(110) is attributed to the fact that the energy is closer to the onset of bulk interband transitions at 3.87 eV.<sup>7</sup>

The crystal-surface and the orientation dependence of the surface-plasmon energies on Ag single crystals was first noted by Tajeddine, Kolb, and Kotz<sup>9</sup> who used an Otto attenuated-total-reflection configuration to measure the dispersion of surface polaritons (coupled surface-plasmon-photon modes having small  $q_{\parallel}$  in the retardation region) on Ag(111) and Ag(110) single crystals in air. They found that the energy of the surface polaritons on the Ag(111) surface is higher than that of the surface polaritons on the Ag(110) surface, and that the energy of surface polaritons on Ag(110) with  $q_{\parallel}$  along  $[1\bar{1}0]$  is higher than that of surface polaritons with  $q_{\parallel}$  along  $[001]$ . Their data are in contrast to our data, which show that the surface-plasmon energy on clean Ag(111) is lower than that on clean Ag(110). We attribute this difference in results to the fact that their measurements were carried out in air and that the higher surface-polariton energy on Ag(111) they obtain is due to surface contamination. This highlights the large sensitivity of the dielectric response in the surface region to the effect of the adsorbates.

Theoretically, the normal modes at the surface can be determined by calculating the reflectivity for  $p$ -polarized light  $R_p$  as a function of  $\omega$  and  $q_{\parallel}$ , and then finding the poles in this function, i.e.,  $R_p(\omega, q_{\parallel}) = \infty$ . For free-electron metals, a dispersion relationship for the surface plasmon has been derived by Harris and Griffin,<sup>10</sup> and by Flores and Garcia-Moliner<sup>11</sup> and can be expressed in the following form:<sup>4</sup>

$$\epsilon^{(B)} + 1 - (\epsilon^{(B)} - 1)(d_{\perp})q_{\parallel} = 0, \quad (1)$$

where  $\epsilon^{(B)}$  is a bulk dielectric constant, and  $d_{\perp}$  is the center of mass of the induced charge density measured with respect to the jellium edge.<sup>4</sup> The third term in Eq. (1) represents the contribution from the induced charge density to the  $z$  component of the dielectric response in the surface region of the metal. In the RPA formulation, with a Lang-Kohn charge-density profile,  $d_{\perp}$  is positive, i.e., the center of mass of induced charge density is outside of the positive charge density,<sup>4</sup> and as a consequence the surface-plasmon dispersion is negative. There have been several theoretical efforts to include the effect of lattice periodicity into the “ $d$  function formalism,”<sup>12,13</sup> but none have taken surface-state and interband transitions into consideration.

Because of the lack of the horizontal mirror plane at the surface, the symmetry of the surface [ $3m$  for Ag(111) and  $2mm$  for Ag(110)] is lower than that of the bulk ( $m3m$ ). The electronic states of the surface reflect this reduced symmetry compared to the bulk states. In

the case of a non-free-electron metal such as Ag, we must take into account contributions to the dielectric response from interband transitions in the bulk, surface-state transitions, and surface-modified-band-state transitions in the surface region. The dielectric response which determines  $R_p(\omega, q_{\parallel})$  and the surface-plasmon energy [i.e.,  $R_p(\omega, q_{\parallel}) = \infty$ ] involves both bulk and surface contributions. It can be written in the following form:

$$\epsilon = 1 + 4\pi\{\chi_f^{(B)} + \chi_f^{(S)} + \chi_o^{(B)} + \chi_o^{(S)}\}, \quad (2)$$

where superscripts  $B$  and  $S$  denote bulk and surface ( $z$ -dependent) contributions, and subscripts  $f$  and  $o$  denote the free-electron and “orbital” (surface-state transitions, interband transitions, etc.) contributions to the electric susceptibility  $\chi$ . The contribution from the first two terms (based on the jellium model) would predict a negative dispersion and a surface-plasmon energy at  $q_{\parallel} \approx 0$  independent of the crystal surface and the direction of propagation. Therefore  $\chi_o^{(B)}$  and  $\chi_o^{(S)}$  must be responsible for the observed dispersion, while only the surface term  $\chi_o^{(S)}$  can contribute to the crystallographic differences in the surface-plasmon energy at  $q_{\parallel} \approx 0$ .

The electric susceptibility is a tensor, and in the case of the Ag(110) surface, the in-plane components of  $\chi^{(S)}$  are anisotropic; whereas, in the case of the Ag(111) surface, the in-plane components are isotropic. It is easy to illustrate the origin of the anisotropic surface dielectric response for Ag(110) following the arguments presented by Pajer<sup>14</sup> using the measured and calculated surface electronic structure of the noble metals.<sup>15</sup> Consider for the purposes of this illustration two high-symmetry points in the surface Brillouin zone of Ag(110), the  $\bar{Y}$  point at the zone boundary in the  $[001]$  direction and the  $\bar{X}$  point at the zone boundary in the  $[1\bar{1}0]$  direction. There are two surface states at  $\bar{Y}$ , one below and one above the Fermi level.<sup>16,17</sup> In contrast, there is only one surface state at  $\bar{X}$ , which lies above the Fermi level. The upper surface state at  $\bar{Y}$ , which is derived from states in the  $s$  band, has even parity along the  $[001]$  direction and the lower surface state, which is derived from states in the  $p$  band, has odd parity in the  $[001]$  direction. The surface state at  $\bar{X}$ , which is largely derived from the  $s$ -band states, has even parity. Optical transitions at  $\bar{Y}$  between the surface states, between the  $p$  band and the upper surface state, between the lower surface state and the  $s$  band, between the  $p$  band and  $s$  band and between the  $d$  band and  $p$  band are all induced only by  $E_y$ . The optical transitions at the  $\bar{X}$  point between the  $p$  band and the surface state and between the  $d$  band and the  $p$  band are induced by  $E_x$ . Therefore, the surface contribution to the electric susceptibility is anisotropic in the plane of the (110) surface. In contrast to the Ag(110) surface, the Ag(111) surface possesses only one surface state which is derived from the  $p$  band at the  $\bar{\Gamma}$  point of the Brillouin zone. Transitions between the surface state and the  $s$  band, between the  $p$  band and the  $s$  band, and

between the  $d$  band and the  $s$  band can be induced by either  $E_x$  or  $E_y$ ; i.e., the dielectric response in the surface plane is isotropic. It is thus evident that, as a result of the markedly different surface electronic structure, the dielectric-response tensors for the two surfaces are quite different.

The experimental data for the surface-plasmon energy and dispersion on the two faces of Ag have clearly shown the importance of understanding the surface contributions to the dielectric response. What is needed now are theoretical calculations of the different contributions to the dielectric response written down in Eq. (2). With a given representation of  $\epsilon$ , the energy- and wave-vector-dependent reflectivity can be determined by the procedure of Feibelman<sup>4</sup> and Appel, Ljungbert, and Lundqvist.<sup>18</sup> The energy of the surface plasmon for given  $q_{\parallel}$  is then obtained as the frequency at which  $R_p(q_{\parallel}) = \infty$ .

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