

Comment on "Surface Plasmon Dispersion of Ag"

The long-wavelength dispersion of the surface plasmon is known to be negative for the simple metals [1], but has been found to be positive and strongly crystal-face dependent for Ag [2–5]. A Letter by Liebsch [6] attributes the positive dispersion of the surface plasmons of low-Miller-index Ag crystal planes to a reduction in the screening of the fluctuating field by $4d$ electrons, as the magnitude of the plasmon wave vector q increases. His argument is based on the notion that screening by the $4d$'s is what reduces the $q=0$ surface plasmon frequency from 6.4 eV, corresponding to the density of "free" $5sp$ electrons in Ag, to the frequency where it is actually observed, 3.69 eV [4]. Liebsch reasons that surface plasmon fields at larger q are more confined to the "selvedge" region where, since $4d$ electron orbitals are smaller than $5s$ and $5p$'s, only the $5sp$ electrons are present. Thus at larger q , the surface plasmon's field is less effectively screened by the $4d$'s, and its oscillation frequency increases. Unfortunately, this intuitively appealing argument conflicts with the experimental observation that the linear dispersion coefficient on Ag(001) [2] is somewhere between 2 and 5 times larger [5] than that for Ag(111) [3].

The nub of the problem is that in Liebsch's model the linear dispersion coefficient is larger if the centroid of the surface plasmon's oscillating charge lies farther outside the spatial onset of d -electron screening, or equivalently, farther outside the first plane of Ag nuclei [7]. If the jellium picture of Ag's surface plasmons is meaningful at all, then since Ag's $5sp$ electron density corresponds to electron gas radius $r_s=3$, the centroid of the oscillating charge lies outside the jellium background edge by 0.8 Å [8]. This result is independent of crystal face because the electron density is a bulk quantity. In contrast, the distance from the jellium background edge to the first layer of Ag nuclei does depend on crystal face. Charge neutrality implies that it must equal half an interlayer spacing for whatever face is exposed [9]. On the close-packed (111) surface, the interlayer spacing is 0.32 Å larger than on the more open (001) plane. Thus d -electron screening begins deeper relative to the centroid of the oscillating charge for the (111) case. In Liebsch's model, if less screening occurs in the surface region, then the dispersion should be more positive. *This is the opposite of what is observed.*

In an earlier paper [10], I focused on just this result, i.e., that deeper-lying d electrons correspond to a *less* positive dispersion coefficient. The fact that the $4d$ -to- $5s$ excitation threshold in Ag lies at 3.86 eV, i.e., not quite 0.2 eV higher than the surface plasma frequency, makes it natural to think of the surface plasmon as a collective mode that is split off the bottom of the $4d$ -to- $5s$ particle-hole excitation band. Accordingly, I considered the relation between the surface plasmon dispersion and the $4d$ -

to- $5s$ excitations induced by the surface plasmon's field. Within a simple perturbative model, I showed that the dispersion coefficient increases with the strength of the s - d coupling. Since this coupling corresponds to a $\Delta l=2$ matrix element, it is zero in an isotropic or cubic environment, i.e., inside a cubic Ag crystal. But it can be substantial near enough to a surface, where the spatial variation of the fields associated with a surface plasmon is rapid.

For Ag(001), this argument means that because the $4d$ electrons lie closer to the centroid of the oscillating, free-electron charge, the probability of $4d$ -to- $5s$ excitation is enhanced and the dispersion coefficient is increased relative to Ag(111) where the $4d$'s lie deeper. Thus, describing Ag's positive surface plasmon dispersion in terms of the magnitude of the matrix element for $4d$ -to- $5s$ excitation leads naturally to the observed crystal-face dependence. The model proposed by Liebsch contains no explicit reference to $4d$ -to- $5s$ transitions induced by the surface plasmon field. This lack of "self-consistency" is the source of the model's qualitatively incorrect prediction of the linear dispersion coefficient's crystal-face dependence.

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