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Effect of surface interband transitions on surface plasmon dispersion: O/Ag(001)

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The effect of surface interband transitions (SIT) on surface plasmon dispersion was investigated by high-resolution electron-energy-loss spectroscopy for Ag(001). We demonstrate that the anomalous linear dispersion on this face, which is at variance with the parabolic form present for the other low Miller index surfaces, is due to a SIT between Shockley states that nearly matches the surface plasmon frequency. The anomaly is eliminated when the substrate undergoes a missing-row reconstruction induced by oxygen adsorption that removes the SIT.

Collective electronic excitations at metal surfaces have always been at the center of considerable interest as they affect a variety of surface properties ranging from photoemission and chemisorption to surface optics.[1–3] The response function of simple metal surfaces to external electric fields[4] was found to be correctly described by the jellium model, which predicts a negative dispersion of the surface plasmon with a parallel wave vector $q_\parallel$, at least for vanishing $q_\parallel$ values. For Ag surfaces, on the contrary, the presence of the *d* electrons reverses the sign of the dispersion.[5] The actual value of the initial slope and the relative importance of higher-order terms in $q_\parallel$ came out to depend on crystal face and, for the (110) surface, on crystallographic direction.[2,8] The positive sign of the initial dispersion was explained by the $q_\parallel$-dependent shift of the surface plasmon frequency with respect to its value for a free electron gas with a density appropriate to Ag (from 6.4 to 3.7 eV at $q_\parallel=0$), induced by the interband transitions involving the *bulk d* bands.[6,7] The face dependence of the dispersion could be reproduced by theory assuming different distances, z_0, of the polarizable medium from the geometric surface plane.[6,3] However, theory was unable to explain the azimuthal anisotropy on Ag(110) and the different shape of the dispersion curve, which is nearly *linear* (possibly with a small negative curvature) for Ag(001) (Refs. 5 and 9), and *parabolic* with a large and *isotropic* quadratic term for the other low Miller index faces.[8] Moreover, a naive identification of the parameter z_0 with the distance of the outermost *d*-electrons plane from the geometric surface plane would lead to a larger initial slope for Ag(111) than for Ag(001), contrary to experiment.

The anomalous behavior of Ag(001) was suggested to be related to the *surface* interband transition (SIT) present at $\bar{X}$,[10–12] which nearly matches the surface plasmon frequency.[5,2] F. Moresco *et al.*[13,14] showed more recently for Ag(110) that the quadratic term of surface plasmon dispersion along ⟨001⟩ is affected by K adsorption while the linear term remains unchanged, at least at low coverage. The dispersion coefficients were, moreover, independent of the K-induced $1\times n$ reconstructions of the substrate geometry. Following the suggestion given in Ref. 5 they attributed the phenomenon to the new surface plasmon decay channel associated with the formation of a surface interband transition (SIT) involving the filled Shockley state at $\bar{X}$ and the empty *p* state of K.

While the influence of *bulk* interband transitions on surface plasmon energy (and hence on the dispersion) is well established, we will prove in this paper that surface plasmon dispersion is affected also by *surface* interband transitions, as the anomalous behavior of Ag(001) can be eliminated by removing the SIT at $\bar{X}$. The destruction of this SIT is achieved by the missing-row reconstruction of the surface, which is induced by oxygen adsorption below room temperature and whose effect is to shift the occupied Shockley state at $\bar{X}$ above the Fermi level. The initial slope of the dispersion is modified too, and becomes smaller than for Ag(111), as predicted by Liebsch's jellium-based theory. Our results suggest therefore that the latter correctly describes the anisotropy of Ag in absence of SIT's, which must however be included for a complete description of the response function at the surface.

Experiments were performed with a self-constructed high-resolution electron-energy-loss spectrometer (HREELS), with a rotatable monochromator which allows one to select the desired momentum transfer. The resolution was set to 15 meV for the clean surface and degradated to 20 meV for the oxygen phases, in order to improve the signal-to-noise ratio. This constraint was particularly important for the O_2 adsorption experiment for which the inelastic count rate was very low. Contrary to the case of O_2/Ag(110) (Ref. 2) the loss peak was, however, still sharp. The integration in reciprocal space, due to the angular acceptance of 2°, is estimated to be about 0.04 Å^{-1}. The experimental apparatus was described in detail in Ref. 15. The Ag(001) sample is a disc of 10-mm-diam oriented to within 0.25° off the nominal plane. It is prepared *in situ* by sputtering and annealing to 400 °C before each experimental run. Surface cleanliness and order were checked by HREELS while surface order and reconstruction were controlled by inspection with low-energy electron diffraction (LEED).

On Ag(001) oxygen adsorbs disorderly below 150 K in a peroxide state.[16] Dissociative chemisorption, occurring above this temperature, was recently investigated thoroughly with LEED and HREELS in Genova, and with x-rays photoemission spectroscopy (XPS) and photoelectron diffraction (XPD) at the ELETTRA synchrotron in Trieste.[17] Two phases were found: (i) *phase I*, consisting of a $2\sqrt{2}\times\sqrt{2}$

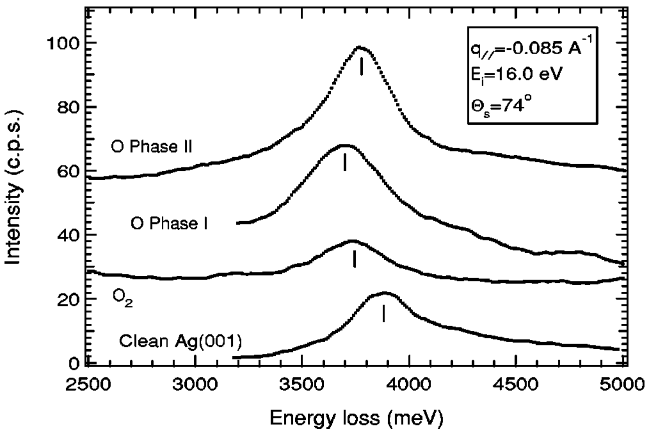

FIG. 1. Sample spectra showing the surface plasmon loss at $q_{\parallel} = -0.085$ Å^{-1} for the different phases of oxygen on Ag(001). The energy resolution of the electron spectrometer is different for the clean and for the oxygen-covered surface. The inelastic count rate of the lowest spectrum is therefore not directly comparable with the others.

superstructure due to a missing-row reconstruction similar to that reported for O/Cu(001) (Ref. 18), and (ii) *phase II*, formed upon heating the missing-row structure above room temperature, and characterized by a restored (1×1) symmetry with the oxygen adatoms sitting in the fourfold hollow sites.

Electron-energy-loss spectra recorded at $q_{\parallel} = -0.085$ Å^{-1} and at impact energy $E_i = 16$ eV for the clean and for the adsorbate-covered surface are shown in Fig. 1. The first data coincide with our previous reports,[5,9] while the loss frequency in the presence of oxygen is lower than for clean Ag(001). Other spectra were recorded for different angles of incidence θ_i to study the dispersion of the surface plasmon. Sample measurements are shown in Fig. 2 for an O_2 overlayer (panel A) and for oxygen adatoms in phase I (panel B). The estimated coverages are $\Theta_{O_2} = 0.15$ ML and $\Theta_O = 0.3$ ML, respectively. Spectra recorded at electron-impact energies E_i of 12 and 14 eV yielded identical results so that we can confidently associate the energy loss corresponding to the maximum of the inelastic intensity to the surface plasmon frequency. The error on it is estimated to be about 10 meV from the spread in the data (see Figs. 3 and 4). The transferred wave vector was then calculated from energy and momentum conservation.[2]

The dispersion curves obtained for unreconstructed substrates, i.e., in the presence of $\Theta_{O_2} = 0.15$ ML of molecular oxygen (data of Fig. 2A), of $\Theta_O = 0.1$ ML of oxygen adatoms in phase II and for clean Ag(001), are shown in Fig. 3. Since within experimental error the quadratic term is compatible with zero for $q_{\parallel} < 0.2$ Å^{-1}, a linear best fit to the data was performed in this range. The so calculated best-fit parameters, reported in Table I, demonstrate that the initial slope of the dispersion curve is smaller in the presence of oxygen. A reduction of the initial dispersion slope was reported also for Cl/Ag(111) where the decrease starts at $\Theta_{Cl} > 0.26$ ML,[19] implying that larger coverages are necessary. The effect was explained qualitatively within the frame of Liebsch's theory[6] as being due to positive charging of the substrate and to the extra screening induced by the Cl layer. We believe this explanation to be valid also here, oxygen being only slightly less electronegative than Cl. The different effectiveness of oxygen admolecules, oxygen adatoms, and chlorine in changing the initial slope is connected with the different adsorption heights and with the different charge transfer [0.5 electron per admolecule for O_2, nearly 1.0 electron per adatom for O (Ref. 20) and for Cl (Ref. 19)].

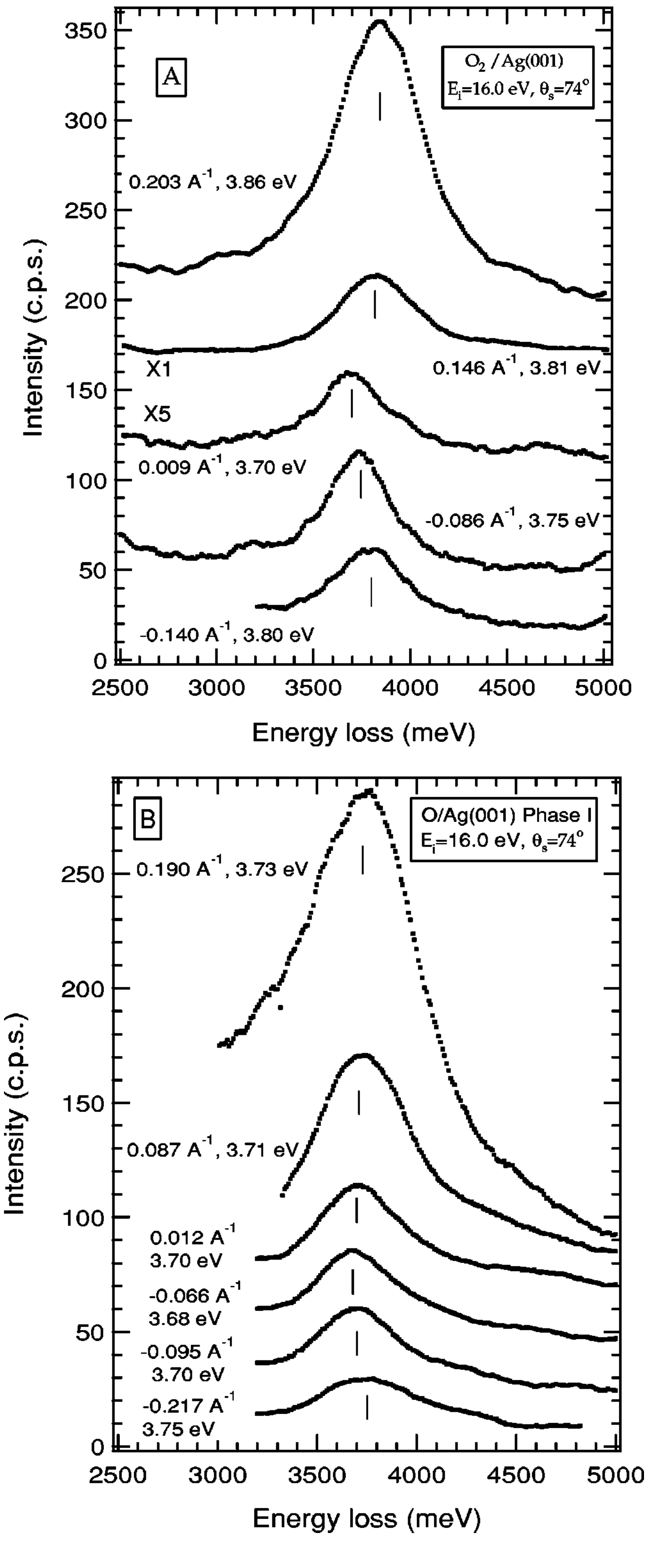

FIG. 2. HREEL spectra recorded at different angles of incidence for (A) the O_2-covered surface and (B) the reconstructed $(2\sqrt{2}\times\sqrt{2})$ O phase.

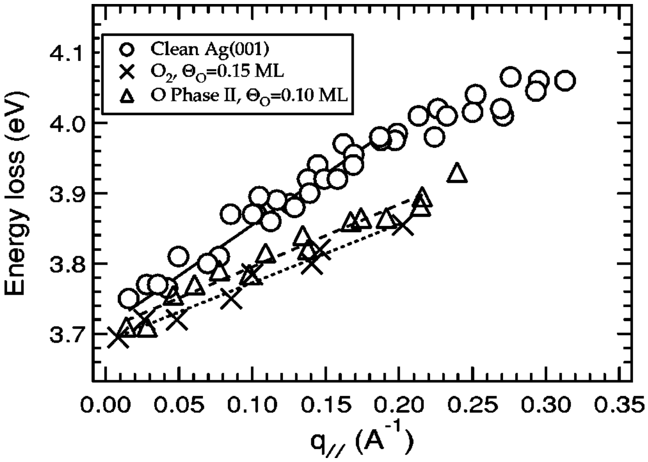

FIG. 3. Comparison of the surface plasmon dispersion in the presence of O_2 and the atomic oxygen of phase II with the clean surface. In all cases the substrate is unreconstructed. The lines are the linear best fit to the data.

TABLE I. Linear best-fit values of the surface plasmon dispersion curve for the the different phases of the unreconstructed surface. The form used in the calculations was $\hbar\omega(0)+Aq_\parallel$, for $q_\parallel < 0.2$ Å^{-1}.

	Θ (ML)	$\hbar\omega(0)$ (eV)	A (eVÅ)
Clean Ag(001)		3.71 ± 0.01	1.45 ± 0.03
O_2/Ag(001)	0.15	3.69 ± 0.01	0.83 ± 0.06
O phase II	0.10	3.71 ± 0.01	0.88 ± 0.05

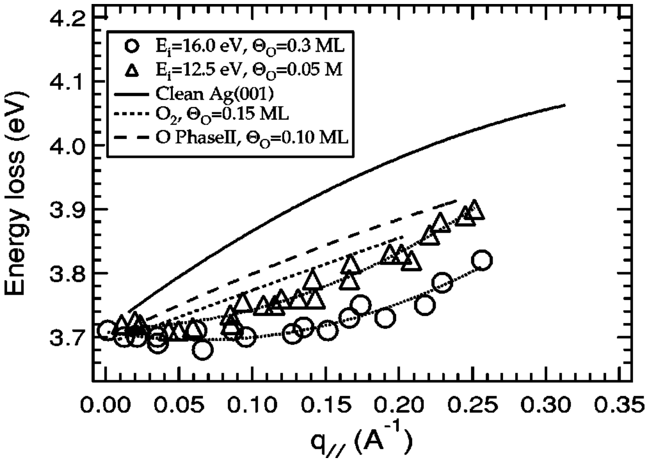

FIG. 4. Surface plasmon dispersion data vs $q_\parallel$ for different coverages of atomic oxygen in phase I. The set for $\theta_O=0.3$ ML corresponds to the $2\sqrt{2}\times\sqrt{2}$ LEED pattern. Parabolic best-fit curves for clean, O_2, and phase II–oxygen-covered surfaces are shown for comparison, too.

The experimental data for phase I (reconstructed substrate) are collected in Fig. 4 vs $q_\parallel$ for two coverages. The dispersion is now qualitatively different with respect to the one observed for oxygen phases on unreconstructed Ag(001) and for Cl/Ag(111). Already at small coverages we see that (i) the initial slope is close to zero or negative and (ii) the dispersion curve has a non-negligible and positive quadratic term. Ignoring the latter term would imply the acceptance of an unreasonable change of the surface plasmon frequency at $q_\parallel=0$ (this quantity is determined by the bulk dielectric function) and a significantly worse agreement with the data.

The best-fit parameters obtained from the data when fitting with a parabolic form are reported in Table II. The quadratic term is negative for the clean surface in accord with previous results;[9] it is still negative but compatible with zero for the unreconstructed oxygen phases; and it becomes definitively positive for the reconstructed surface. Within error it is now the same as for the other low Miller index surfaces [3.1 ± 0.5 eVÅ^2 against 3.5 ± 0.2 eVÅ^2 for both (110) and (111) (Ref. 8)]. Moreover, its initial slope is nearly zero or even slightly negative, i.e., definitely smaller than for Ag(111), for which it reads $+0.43\pm0.02$ eVÅ. The initial slope for the different Ag faces follows now the same trend as the distance of the *d* electrons from the geometric surface as predicted by the ‘‘naive’’ interpretation of Liebsch’s theory and the apparent contradiction between experiment and theoretical forecast is eliminated.

The effect of adsorption-induced reconstruction on surface plasmon dispersion could have the following origins.

(i) Oxygen might affect the *d* bands at the surface and remove the Tamm state at $\overline{M}$ (Ref. 21).

(ii) It might affect the *s* band of Ag either by adding new states or by removing the Shockley surface states.

(iii) It might shift the surface states thus removing the decay channel for the surface plasmon associated to the interband transition at $\overline{X}$.

We exclude the first hypothesis because the quadratic term is *identical* for Ag(111) and Ag(110), which have totally different projections of the bulk *d* bands, while a Tamm state should be present also on Ag(111) at $\overline{M}$.[22,11] For the same reason we expect that the hybridization of the O $2p$ state with the $4d$ bands, which is stronger for phase I than for phase II,[17] should play only a minor role.

We exclude the second guess as the oxygen-induced reduction of the spectral density of the Shockley states is expected to occur also for phase II, whose dispersion remains, however, linear. The effect should be, moreover, negligible at low coverage, contrary to experimental evidence. It must therefore be connected to the reconstruction of the Ag substrate, but since for K/Ag(110) (Ref. 13) no change in surface plasmon dispersion was observed at the onset of the missing-row reconstruction, the modification of surface geometry is not sufficient.

We propose therefore that the relevant effect is connected to the elimination of the interband transition at $\overline{X}$, which is nearly degenerate with the surface plasmon frequency. Such

TABLE II. Parameters of the best-fit function $\hbar\omega(0)+Aq_\parallel+Bq_\parallel^2$ for the dispersion curve of the surface plasmon on clean and oxygen-covered Ag(001).

	Θ (ML)	$\hbar\omega(0)$ (eV)	A (eVÅ)	B (eVÅ^2)
Clean Ag(001)		3.71 ± 0.01	1.73 ± 0.13	-1.9 ± 0.4
O_2/Ag(001)	0.15	3.69 ± 0.01	0.86 ± 0.20	-0.1 ± 1.0
O phase II	0.10	3.70 ± 0.01	1.1 ± 0.2	-0.9 ± 0.7
O phase I	0.05	3.71 ± 0.01	0.0 ± 0.1	3.1 ± 0.5
O phase I	0.3	3.71 ± 0.01	-0.4 ± 0.1	3.1 ± 0.5

modification of the surface excitation spectrum is caused by the shift to higher energy of the Shockley surface states due to the reconstruction-induced change of the density of the outermost surface layer.[23] Such effect was demonstrated experimentally to take place for H/Ni(110) (Ref. 24) and for Na/Cu(110).[25] The removal of the interband transition at $\overline{X}$ for the missing-row reconstructed Ag(001) surface is confirmed by a recent *ab initio* calculation by Cipriani, Dal Corso, and Baroni.[26] The mere presence of oxygen would on the contrary have the opposite effect of stabilizing the surface states.[23,26] The reconstruction-induced change of the surface Ag density is thus essential to remove the interband transition.

In conclusion we have shown that the form of surface plasmon dispersion in the presence of *d* electrons is determined not only by the bulk interband transitions associated with the *d* electrons but also by the, so far neglected, *interband transitions between surface states* (not necessarily of *d*-type). Those transitions whose energy is close to the one of the surface plasmon are particularly important. The shortcomings of the jellium-based theory[6] to describe the anisotropy of the dispersion for the different Ag surfaces and the anisotropy with respect to the crystallographic direction for Ag(110) is therefore explained by the fact that surface states are neglected.

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