

Reflectance anisotropy spectra of Cu and Ag (110) surfaces from *ab initio* theory

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Reflectance anisotropy spectra of Cu and Ag (110) surfaces are obtained by *ab initio* calculations. We disentangle the effects of the intraband and interband parts of the bulk dielectric function in the spectra, splitting them further into components stemming from bulk and surface states. As in the case of semiconductor surfaces, transitions across bulk states yield large contributions. A good description of experimental results is obtained. We find evidence of a small surface dielectric anisotropy due to intraband transitions.

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Reflectance anisotropy spectroscopy (RAS) is a powerful technique for probing the optical properties of surfaces. Reflectance anisotropy is the relative difference of the reflectivities measured with light polarized along two perpendicular axes on the surface. Since the pioneering work by Aspnes¹ in 1985, the technique has found widespread applications in semiconductor surface science; however, the first RA spectrum of a metallic surface appeared, for Ag(110),² in 1993. This research has recently gained renewed impulse.^{3,4,6–10} However, a microscopic interpretation of RA spectra in terms of electronic transitions among surface and/or bulk states is still missing, which limits the potential of the technique itself.¹¹ This state-of-the-art situation calls for a sound interpretation of RAS based on microscopic calculations. From the theory side, however, only two extreme models are available: the semi-infinite jellium model,¹² which yields no RA, and an interacting-dipole model (the so-called *swiss cheese* model), which is currently used to describe experimental data.^{2,5,6} *Ab initio* effective one-electron calculations have recently begun,^{13,14} but no clear interpretation of the experiments has appeared so far.

In this paper we present the RA spectra of Cu and Ag (110) surfaces obtained by an *ab initio* one-electron calculation within density-functional theory¹⁵ (DFT) using the local-density approximation¹⁶ (LDA). This theoretical approach is the most effective and widely used *ab initio* treatment of the electronic properties of solids when many-body effects are neglected.

We analyze the structures in the RA spectra in terms of optical transitions among surface or bulk states. This is an issue of fundamental interest since it is related to the efficiency of optical spectroscopy in detecting surface states. As in the case of semiconductor surfaces,¹⁷ we show that surface-perturbed bulk states yield important contributions.

The surface reflectivity anisotropy in the present case is $\Delta r/r = 2(r_{[1\bar{1}0]} - r_{[001]}) / (r_{[1\bar{1}0]} + r_{[001]})$, where $r_{[1\bar{1}0]}$ and $r_{[001]}$ are the reflectivities measured with light polarized along the two symmetry directions of the (110) surface. According to the microscopic theory of surface optical properties¹⁸ the RA spectrum for a semi-infinite crystal is given by¹⁹

$$\text{Re} \left\{ \frac{\Delta r}{r} \right\} = \frac{4\pi\omega d}{c} \left(\frac{(\epsilon_1^b - 1)\Delta\epsilon_2}{(\epsilon_1^b - 1)^2 + (\epsilon_2^b)^2} - \frac{\epsilon_2^b \Delta\epsilon_1}{(\epsilon_1^b - 1)^2 + (\epsilon_2^b)^2} \right), \quad (1)$$

where ϵ^b is the bulk dielectric function and $\Delta\epsilon$ is the surface dielectric anisotropy (SDA) (subscripts 1,2 refer to the real and imaginary parts, and the ω dependence is understood). $\Delta\epsilon$ is related to $\epsilon_{[1\bar{1}0]}(z, z'; \omega)$ and $\epsilon_{[001]}(z, z'; \omega)$, the dielectric susceptibilities of the surface for light polarized along $[1\bar{1}0]$ and $[001]$, by

$$\Delta\epsilon(\omega) = \frac{1}{d} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dz dz' [\epsilon_{[1\bar{1}0]}(z, z'; \omega) - \epsilon_{[001]}(z, z'; \omega)], \quad (2)$$

where d is the thickness of the surface layer.²⁰

Self-energy, excitonic, and local-field effects can in principle be included in the dielectric susceptibilities.²¹ They are known to be rather important in the optical properties of semiconductors,²² although they cancel each other to some extent; their relevance in the case of metals is still unclear. For this reason and since they are difficult to account for, we neglect them altogether. With this approximation $\Delta\epsilon$ can be obtained from slab calculations in terms of one-electron transitions.¹⁷

It is important to realize that SDA and RA are not equivalent. On the one hand, one can determine the SDA from experiments only if the *complex* $\Delta r/r$ [not only its real part given by Eq. (1)] is known [see Eq. (2) of Ref. 3]; on the other hand, RA structures, although arising from the SDA in the numerators of Eq. (1), can be severely affected by the denominators, i.e., by bulk effects. In particular, when $\epsilon_1^b(\omega) = 1$, the second term on the right-hand side (RHS) of Eq. (1) can have strong resonances, even though $\Delta\epsilon_1$ is small and smooth. In the following, we try to distinguish, in the RA spectra, between the structures arising from the SDA and those arising from bulk effects. We will show that the deep RAS minimum of Ag(110) at 3.8 eV [see Fig. 2(a)]

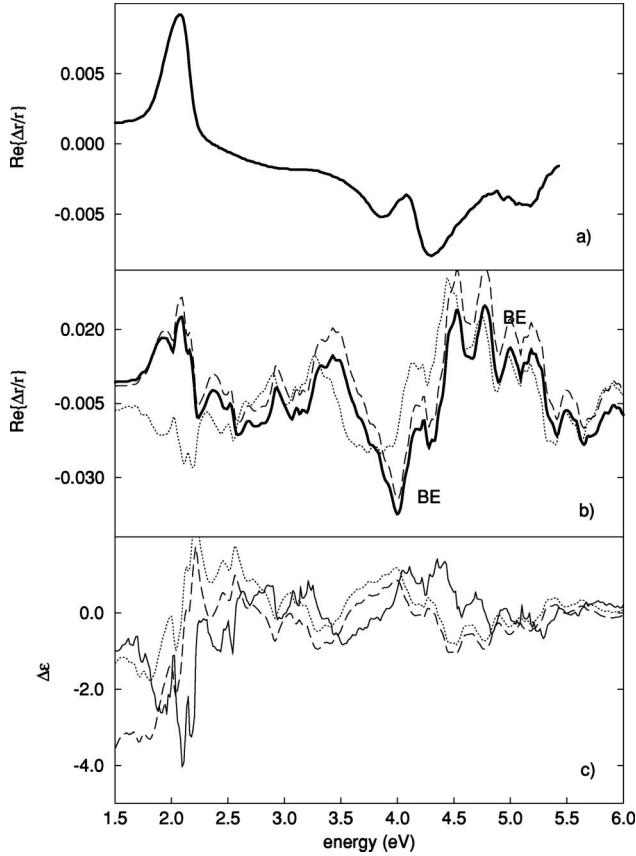


FIG. 1. RAS of clean Cu(110): (a) experiment from Ref. 8 and (b) present calculation with (bold) and without (dotted) the Drude component in ϵ^b . The dashed curve also includes intraband surface anisotropy (see text), BE labels bulk resonances. (c) Real (dashed) and imaginary (solid) parts of the calculated interband surface dielectric anisotropy (SDA). The dotted line is the real part of SDA including the intraband surface anisotropy. A Lorentzian broadening of 10 meV is included in the calculated spectra.

originates from bulk effects, while that of Cu(110) above 4 eV [see Fig. 1(a)] has a mixed character.

The dielectric function of metals contains contributions from interband and intraband transitions.²³ We calculate *ab initio* only the interband parts of $\Delta\epsilon$ and ϵ^b , whereas the intraband term of ϵ^b is computed as $\epsilon_1^{b,D} = 1 - \omega_p^2 \tau^2 / (1 + \omega^2 \tau^2)$ and $\epsilon_2^{b,D} = \omega_p^2 \tau / \omega (1 + \omega^2 \tau^2)$.²⁴ Here the plasma frequency ω_p and the relaxation time τ are taken from experiments.²⁴ This is justified by the fact that τ can hardly be computed *ab initio* and that a test calculation of ω_p agrees well with experimental results.²⁵ An anisotropic intraband Drude-like contribution to $\Delta\epsilon$ cannot be excluded *a priori*. However, for frequencies $\omega \gg 1/\tau$, it affects only the real part of $\Delta\epsilon$, which, according to Eq. (1), is important in determining the RA only when ϵ_2^b is different from zero. This happens above the threshold of bulk interband transitions (about 2 eV in Cu and 3 eV in Ag, respectively) where the Drude tail is already small and structureless. Therefore, we neglect the intraband surface anisotropy altogether. Possible errors induced by this approximation are discussed later.

The computation of the electronic properties and interband part of the dielectric functions has been carried out

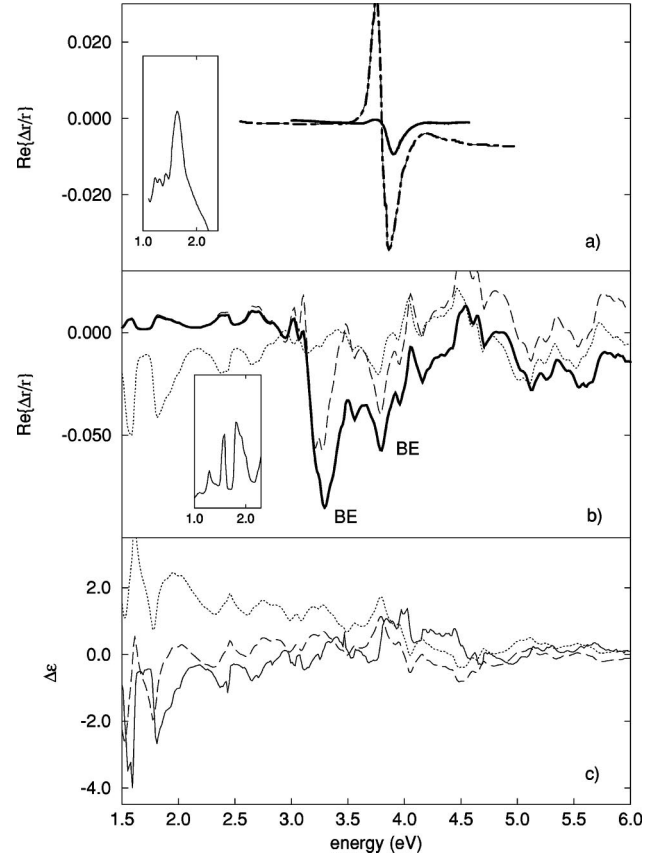


FIG. 2. The same plots as in Fig. 1 for Ag(110). The experimental data in (a) are from Ref. 3 (dot-dashed line) and from Ref. 10 (solid line). The insets show the low-energy peak on a magnified scale.

self-consistently using the full potential (FP) version²⁶ of the linear muffin tin orbital (LMTO) method²⁷ within the DFT-LDA, with a repeated slab scheme including 11 atomic plus 6 vacuum layers. k -space integrations are performed with the analytical tetrahedron method.²⁸ Meshes as dense as 752 and 256 k points in the irreducible bulk and surface Brillouin zone, respectively, give converged values for the dielectric functions calculated in terms of the matrix elements of the momentum operator among occupied and unoccupied electronic states.²³ The relaxed, unreconstructed geometry of the Cu and Ag (110) surfaces²⁹ has been taken into account. In order to keep all the details of the calculated spectra, we use a Lorentzian broadening as small as 10 meV.

In Fig. 1(a) we report the experimental RA data for Cu(110) (Ref. 8) and in Fig. 2(a) those for Ag(110).^{3,10} The RA spectra are characterized by a low- (<2.5 eV) and high- (between 3 and 5 eV) energy part, according to the prominent spectral features. A roughly bell-shaped peak appears in the low-energy part for both metals, whereas the high-energy structures look quite different in either metal. These peaks and structures have been recently ascribed to transitions among surface states.^{3,8} We will show below that this is true only for some of them.

In Fig. 1(b) for Cu and in Fig. 2(b) for Ag, we have plotted the calculated RA [Eq. (1)], with and without the Drude contribution in ϵ^b . This shows how the Drude term in

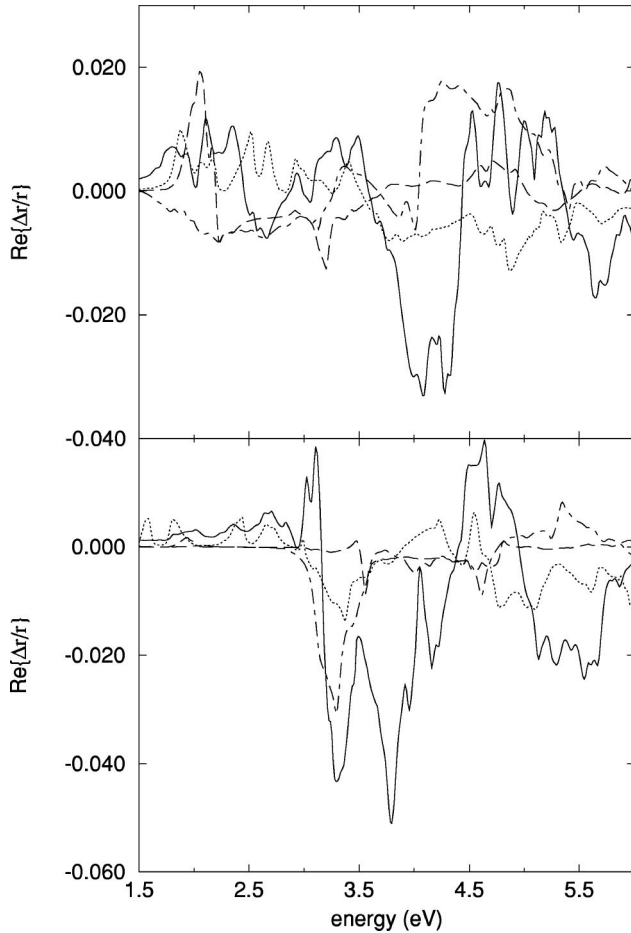


FIG. 3. Different contributions to the RA of Cu(110) (top) and of Ag(110) (bottom). Solid line: bulk-state to bulk-state transitions (BB). Dashed line: surface-state to surface-state transitions (SS). Dotted line: bulk-state to surface-state transitions (BS). Long-short dashes: surface-state to bulk-state transitions (SB). A Lorentzian broadening of 10 meV is included in the spectra.

ϵ^b essentially determines the sign of the RAS peaks at low energies. $\Delta\epsilon_1(\omega)$ and $\Delta\epsilon_2(\omega)$ are plotted in Figs. 1(c) and 2(c) for Cu and Ag, respectively, in order to illustrate, by comparison with the RA in panels (b), the occurrence of bulk effects in the latter. Finally, to ascribe the observed structures in the RA spectra either to bulk- or surface-state transitions, we have plotted in Fig. 3 the four separate contributions from bulk-to-bulk (BB), surface-to-surface (SS), surface-to-bulk (SB), and bulk-to-surface (BS) state transitions.³⁰

Let us now discuss our results. Starting with Cu and inspecting Fig. 1(c), we see that the structures appearing in the real and imaginary parts of the SDA occur also in the RA spectrum albeit with reversed sign [Fig. 1(b)], as far as $\epsilon_1^b(\omega) < 1$, which is generally true within the range of our figures. Moreover, the calculated $\epsilon_1^b(\omega)$ (not shown here) is close to 1 at 4.0 and 4.8 eV, which strengthens the negative (positive) RA resonance at 4 eV (close to 5 eV). Hence, these resonances (labeled BE) are partially due to bulk effects. Comparing Fig. 1(b) with Fig. 3 (upper panel) one sees that the low-energy peak at ≈ 2 eV comes from SS interband transitions. We confirm that such transitions occur among

surface states at and near point \bar{Y} of the surface BZ.⁸ The other structure close to 4 eV is due, as inferred from Fig. 3, to BB and SB transitions in $\Delta\epsilon$, enhanced and shifted by the bulk contribution of the denominators. This structure is not, therefore, due to interband transitions from surface resonances to surface states at \bar{X} as previously hypothesized.⁸ By comparing the calculated [Fig. 1(b)] and measured [Fig. 1(a)] RA spectra we see a rather good agreement for both the low- and high-energy structures. In particular, the experimental minimum at about 4.2 eV is well described by the calculated one at 4 eV and the measured maximum at 4.8 by the calculated doublet centered at 4.6 eV. The *swiss cheese* model^{2,5} yields a worse description of all the structures. We recall that the small broadening and the neglect of many-body effects in our calculation are expected to hamper a more quantitative agreement with experimental data. The RA in the experiment is 3 or 4 times weaker than in the calculation, as happens at some semiconductor surfaces.³² This can be due to the presence of steps and other imperfections at real surfaces.

Looking at Fig. 2(c), we see that the SDA of Ag(110) is less structured than that of Cu. Also for Ag(110), Eq. (1) reverses, in the RA spectrum [Fig. 2(b)], the sign of the SDA structures [Fig. 2(c)]. Notice that, on the low-energy side, only the imaginary part of $\Delta\epsilon$ effectively contributes in Eq. (1), since ϵ^b is almost completely real. The calculated $\epsilon_1^b(\omega)$ (not shown here) is close to 1 at (i) 3.3 and (ii) 3.8 eV: (i) yields the main feature of the spectrum, the large dip at 3.3 eV, where the SDA is small and structureless, while (ii) yields the mixed SDA-bulk structure at 3.8 eV (both labeled as BE). Hence, the main structure of the calculated spectrum, corresponding to the experimental one close to 3.8 eV, is mostly due to a bulk effect. Comparing the total RA with the partial contributions plotted in Fig. 3 (lower panel), we see that the low-energy peak is due to SB transitions, whereas the high-energy structures are induced by BB, SB, and BS transitions.

Our calculated RA spectrum for Ag in Fig. 2(b) also compares satisfactorily with the experiments, apart from a shift in the high-energy structure of about 0.5 eV towards lower frequency³¹ (a similar—albeit smaller—shift occurs also in Cu). This discrepancy, occurring also in Ref. 33, must be due to the underestimation of transition energies in DFT. The line shape of this structure is in good agreement with that obtained in intensively sputtered samples [solid line in Fig. 2(a)].¹⁰ A double-peak structure [dot-dashed line in Fig. 2(a)] is instead observed after a few sputtering cycles.^{3,10} This double-peak structure, well reproduced by the *swiss cheese* model,^{2,5} is absent in our *ab initio* calculations that do not include the long-ranged local-field effect. In the *swiss cheese* scheme the noble metal is modeled by a composite medium made by a jelliumlike background (the *sp* electrons) screening the embedded charged spheres, centered about ions carrying dipoles (due to the *d* electrons). The main shortcoming of this model is that the surface dipoles are assumed to have the same polarizability as bulk ones. The effect of the reduced symmetry of the surface on the dipole-dipole interac-

tion yields a derivativelike RA line shape similar to the experimental one. We speculate that its absence at surfaces treated by several sputtering cycles^{6,10} may be due to the roughening of the surface, which destroys the long-range order and the effect of dipolar interactions. The low-energy peak never shows up in *swiss cheese* model calculations.^{2,6,10}

A possible anisotropy in the plasma frequency, as mentioned before, may induce an intraband term in the SDA. Such anisotropy should only affect $\Delta\epsilon_1$, adding a Drude-like term (neglected in our calculation) to the contribution of interband transitions (treated accurately in our calculation). In fact, the SDA's of these surfaces have been extracted from experiments in Refs. 3 and 9. The imaginary parts are in good agreement with our findings; the real parts, however, are systematically lower. This discrepancy can be fixed by embodying a Drude-like anisotropic term $-\Delta\omega_p^2/\omega^2$ in $\Delta\epsilon_1$. We have assumed a relative anisotropy in the plasma frequencies of 3% and 5% in Cu and Ag, respectively, to fit the experimental data. We obtain the real parts shown by long-dashed lines in Figs. 1(c) and 2(c), which compare favorably with the experimental results. This demonstrates that an anisotropic intraband contribution to the SDA does indeed occur. However, the RA is poorly affected by this anisotropy as can be inferred by comparing the dashed and full curves in Figs. 1(b) and 2(b), calculated with and without the intraband anisotropy term, respectively.

To summarize, we have calculated *ab initio* the RAS spectra of Cu and Ag (110) within the DFT-LDA. The peaks observed at low energy are produced by interband transitions involving surface states. Structures observed at high energy are not, however, due to pure surface-to-surface state transitions, but to transitions across bulk states (and to mixed transitions in the case of Ag), whose strength and position are mostly determined by the vanishing of the denominators in Eq. (1), i.e., by a bulk effect. We find good agreement between our calculations and experimental data, with the exception of the line shape of the higher-energy structure in Ag(110). Local-field effects are probably needed to explain this line shape, as suggested by the good performance of the *swiss cheese* model in this case. Finally, we found evidence of some surface anisotropy arising from intraband transitions in the surface dielectric functions, with little effect on the RA.

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³⁰A state is surface or bulk according to the criterion (Ref. 17) of considering it as surface if its localization on the two outermost

layers of each surface is larger than a given threshold $T=0.5$ (4/11 being the surface localization of an equally distributed state).

³¹The occurrence of $\epsilon_1^b(\omega)=1$ at about 3.7 eV is related to the onset of interband transitions (Ref. 24). This occurs at 3.3 eV in

our calculations, 0.5 eV lower than in the experiment (Ref. 24).

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