

***Ab initio* calculation of depth-resolved optical anisotropy of the Cu(110) surface**P. Monachesi,^{1,2} M. Palummo,² R. Del Sole,² A. Grechnev,³ and O. Eriksson³¹*Dipartimento di Fisica - Università dell'Aquila and Istituto Nazionale per la Fisica della Materia, I-67100 L'Aquila, Italy*²*Dipartimento di Fisica - Università di Roma, "Tor Vergata" and Istituto Nazionale per la Fisica della Materia, I-00133 Roma, Italy*³*Condensed Matter Theory Group, Physics Department, Uppsala University, S-7512 Uppsala, Sweden*

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We calculate the surface dielectric anisotropy (SDA) and the reflectance anisotropy of the relaxed Cu-(110) surface using the *ab initio* self-consistent full potential linear-muffin-tin orbital method within the local-density approximation. Besides interpreting the spectra in terms of transitions involving surface and/or bulk states, we carry out a depth depending scanning of them, from surface to bulk, with the resolution of one atomic layer. We show that the SDA mainly arises in the vacuum region above the surface and in the first atomic layer.

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I. INTRODUCTION

The physics of surfaces and interfaces finds its interest on potential technological applications though being of fundamental interest in itself. The breaking of translational symmetry, brought about by the surface, opens the possibility of the formation of new electronic states (surface states) absent in the bulk. Semiconductors surface physics, challenged by the possible applications in electronics, started a couple of decades before the research on metallic surfaces. In this framework, the interaction of light with matter has enormous practical applications. Therefore the optical properties of layered materials are of primary importance. In its early steps, surface physics focused on basic questions, like the spectroscopic characterization of surface states.¹ More recently, much experimental work is done on the dependence of electronic, magnetic, and optical properties on the composition of interfaces. This drives theorists toward a morphology-dependent analysis of the layered materials.

The dielectric function $\epsilon(\omega)$, i.e., the linear response of a solid to an electromagnetic perturbation, is the quantity to be known for the interpretation of many optical properties, like reflectivity, conductivity, dichroism (in magnetic materials), and related quantities, e.g., the loss function. Therefore theoretical investigations aim to evaluate $\epsilon(\omega)$ to obtain directly measurable optical quantities. An experimental, powerful technique used so far for the investigation of surfaces is the reflectance anisotropy spectroscopy (RAS) that takes advantage of the anisotropy introduced in a cubic solid by the surface. In a RAS experiment one measures, as a function of energy, the reflectivities along two inequivalent directions on a given surface of a properly polished sample. The difference Δr of these two reflectivities, normalized to the total reflectivity r , gives the complex reflectance anisotropy $\Delta r/r$. This quantity, embodying the properties of bulk and surface electronic states, may be further analyzed through theoretical models^{2,3} and by *ab initio* calculations.⁴

A well-known formula, derived from the microscopic theory of electromagnetic interactions in matter,⁵ is normally used to interpret RAS experiments. It is given by²

$$\operatorname{Re}\left(\frac{\Delta r}{r}\right) = \frac{4\pi\omega d}{c} \operatorname{Im}\left(\frac{\Delta\epsilon}{\epsilon^b - 1}\right), \quad (1)$$

where $\Delta\epsilon$ is the surface dielectric anisotropy (SDA) and ϵ^b is the bulk dielectric function, and the ω dependence is understood. The SDA is given by

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

where $\epsilon_{ij}(z, z'; \omega)$ is the dielectric susceptibility tensor of the interface.⁵ The thickness of the surface layer d is not a well defined quantity, although it is expected to be of the order of a few angstroms. Anyway, it plays no role in Eq. (1), since it cancels with the denominator of Eq. (2). It is here retained in order to deal with a dimensionless SDA. The x and y axes are the principal directions of the surface dielectric tensor in the surface plane. Equation (1) (and its imaginary counterpart) allows one to extract the SDA from the measured reflectance and bulk dielectric function, as recently done for Cu and Ag (110) surfaces.⁶ Bulk effects are important ingredients of Eq. (1), for the presence of the bulk dielectric function in the denominator.⁷ The understanding of bulk effects is crucial for the correct interpretation of the RAS in metals as pointed out by some authors⁸ and explained quantitatively in a recent paper.⁴ In metals the dielectric function is due to two kinds of electronic transitions: (i) interband transitions between occupied and unoccupied electronic states of different bands, as in semiconductors; (ii) intraband transitions between occupied and unoccupied states within the same band, obviously absent in semiconductors. As it is well known from the elementary theory, intraband transitions are responsible for the so-called Drude tail at very low energy, whereas the interband ones determine the remainder of the spectrum.

The relatively simple definition of the RA, Eq. (1), contrasts with the need of a complex theoretical apparatus for its interpretation, on one side, and with a strong dependence of the spectra on the treatment of the surface, on the other side. This latter aspect has blown up in the last years and is the subject of intense experimental investigations⁹ that, in turn, challenge the theorists.

Very recent results have shown⁴ how to answer theoretically the question of which peaks in the RA spectra of Cu and Ag (110) surfaces originate from transitions among surface states, bulk states, or both. It is usually assumed that the

dielectric susceptibility is different from its bulk (isotropic) form only close to the surface. This does not exclude the contribution of transitions involving bulk states, since these are present also in the surface region, where their wave functions are modified and made anisotropic by the perturbation due to the surface. A tight-binding calculation for GaAs(110) has shown that the integrated $\Delta\epsilon$ calculated for a slab of 11 layers is very similar to that of a slab of 31 layers, the latter being almost undistinguishable from that of a slab of 93 layers.¹⁰ Hence the contribution to the SDA is expected to come from the first few (four or five) layers below the surface. It would be interesting to check whether or not this is true also for noble metals and, moreover, to have a layer-by-layer picture of the anisotropy. This is the main goal of this work.

We exploit the local character of the linear muffin-tin orbital (LMTO) approach, already used in Ref. 4, to produce such a spatially resolved picture of the surface anisotropy. In so doing, we will find that the RAS of Cu(110) originates in the topmost layer and in the vacuum above it.

The paper is organized as follows. In Sec. II we present the calculation of the electronic structure of bulk Cu and of the Cu(110) surface obtained by the full potential (FP)-LMTO method within density-functional theory–local-density approximation (DFT-LDA).¹¹ We discuss the band structure in terms of electronic states with surface or bulk character. In Sec. III we calculate the dielectric functions $\epsilon(\omega)$ of the surface and bulk. Thanks to the flexibility of the code, a few *ad hoc* implementations enable us to analyze the dielectric function according to two different criteria: (i) bulk or surface character of the initial/final states included in the interband transitions, (ii) layer-by-layer contribution to $\epsilon(\omega)$. We can say that (i) is a spectroscopic criterion, since it helps in determining the spectrum of surface states; (ii) is instead a local criterion, since it determines the regions where the anisotropy arises, summing up over all initial and final, surface or bulk states. The SDA and RAS spectra are calculated and discussed in Sec. IV. In Sec. V we summarize our results, compare them with the experiments, and draw the conclusions.

II. ELECTRONIC STRUCTURE OF CU (110) SURFACE

The electronic properties of a solid limited by a surface may be described, to a good approximation, by the so-called *repeated slab* scheme that allows one to apply the same *ab initio* calculation techniques successfully adopted for bulk materials. This scheme consists in the construction of a unit cell of an arbitrarily fixed number of atomic layers symmetrically terminated by an arbitrarily fixed number of empty layers (the *vacuum*) along the direction perpendicular to the surface. The unit cell is then repeated to infinity, as in the bulk. The unit cell adopted in the present calculation has basis vectors a_1 , a_2 and a_3 . a_1 and a_2 are of length $\sqrt{1/2}$, 1, respectively, along the directions $[110]$ (x), $[001]$ (y) in the (110) surface of an fcc structure. a_3 is orthogonal to the (110) surface and of length $8/\sqrt{2}$. The interlayer distance is $d=1/2\sqrt{2}$ (bulk value) and all lengths are in units of the cubic lattice constant a . The slab geometry must satisfy

some criterion of convergence, depending on the sought for quantity.

As long as the band structure is concerned, we have found that a unit cell consisting of 11 atomic layers plus 6 vacuum layers is a good choice. In fact, tests of this slab configuration against slabs with 7, 11, and 13 atomic layers¹² but with only 4 vacuum layers yield convergence in the band structure already for 11 layers. The introduction of 6 vacuum layers was necessary to reduce the interactions of surface states through the vacuum region, appearing as spurious band splittings in the case with only 4 vacuum layers. This slab size fulfills satisfactorily also the convergence of the total dielectric functions along the two surface directions. Therefore we perform the analysis of the overall optical properties, including the separation of optical transitions due to surface states or bulk states, within this slab configuration. We find results in good agreement with the experiments, as shown below.

On the other hand, the determination of the spatial localization of the SDA within the cell requires a higher accuracy. In fact, to ensure that the innermost layer shows, to a satisfactory extent, properties of the bulk whereas the layer just below the vacuum describes surface properties, we had to build up a slab of 21 atomic layers, keeping the number of vacuum layers equal to 6.

The FP version¹³ of the LMTO (Ref. 14) method within the LDA approximation¹¹ scheme for the exchange-correlation potential is used to calculate the electronic and optical properties presented here. The unit cell is divided into muffin tin (MT) spheres, where the atoms are centered, and an interstitial region surrounding the spheres. In the FP version, the potential is computed without simplifying approximations in the interstitial region, at variance with the original LMTO model.¹⁴

The basis functions are the so-called MT orbitals that are given by two different parts: that within the sphere and that in the interstitial region. These two parts match continuously at the MT sphere boundary. Therefore a wave function (no matter if bulk or slab), made up by MT orbitals, has contributions from the MT spheres and from the interstitial region. We remind that the MT sphere is supposed to preserve more the atomiclike properties of the potential and wave function with respect to the interstitial region. The latter is, in fact, affected by the presence of the surrounding atoms. This separation is intrinsic to the MTO method and in the case of real bulk calculations is irrelevant to conclusions of physical interest. In the slab case, instead, the interstitial region, where there are no MT spheres, includes also the volume occupied by the the vacuum layers which, of course, is not equally distributed in the slab at variance with a plain bulk calculation. We shall come back to this point when discussing the spatial properties of the dielectric function. Finally, the exchange-correlation part of the potential is computed in the scheme of von Barth and Hedin.¹⁵ Self-consistency of the potential is achieved with convergence of 1 part over 10^5 . Brillouin-zone integrations are performed with Gaussian smearing using regular meshes of 10^2 k points and 10^3 in the surface and bulk irreducible Brillouin zone, respectively.

The (110) surface of Cu does not reconstruct but undergoes a relaxation of the two outermost layers.^{16–19} In the

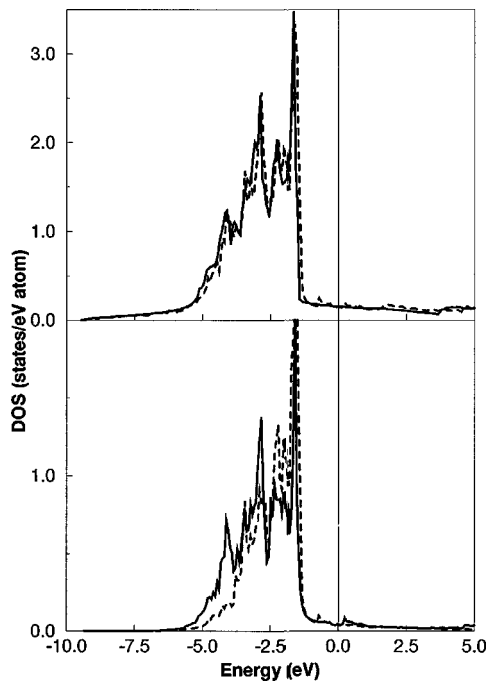


FIG. 1. Total (top) and partial (bottom) densities of states of the Cu slab. In the top panel the total DOS of the 11-layer slab (dashed), normalized to one atom, is compared to the analogous quantity in the bulk (solid). In the bottom panel we report the d -partial DOS of the same slab the surface atomic layer (dashed) and for the bulk atomic layer (solid), respectively. The partial DOS includes the interstitial (with vacuum) contribution. The vertical thin line at zero energy marks the Fermi level.

present work the lattice constant is $a = 6.84$ a.u. and the relaxation amounts to a contraction of the distance among first and second layer (d_{12}) of $\approx 11\%$ and an expansion of 2.4% of the distance among second and third layer (d_{23}). These values are close to the experimental ones in Ref. 17 and to the results of recent calculations.^{18,19} We have performed calculations for both unrelaxed and relaxed surfaces finding, from comparison of the total energies, that the relaxed structure is indeed slightly more stable than the unrelaxed one. We checked further that the RAS, calculated with the relaxation mentioned above, is almost undistinguishable from that calculated using the *ab initio* geometry of Ref. 18 and only slightly different (blueshifted) with respect to the unrelaxed surface. We have carried out calculations also for a much larger relaxation (about trice the values assumed for d_{12} and d_{23} given above) which leads to the suppression of the low-energy surface peak and to a RAS line shape at higher energies in strong disagreement with the experiment.

Integration over the reciprocal space is performed with the linear tetrahedron method²⁰ to obtain, e.g., the density of states and the dielectric function (see the next section). In the upper panel of Fig. 1 we report the total density of states (DOS) of the Cu slab and of the bulk for comparison. By inspection one can see that the effects of the surface in the DOS are a shift of the occupied states toward higher energies with respect to the bulk and the introduction of additional states represented by small bumps in the flat region of the

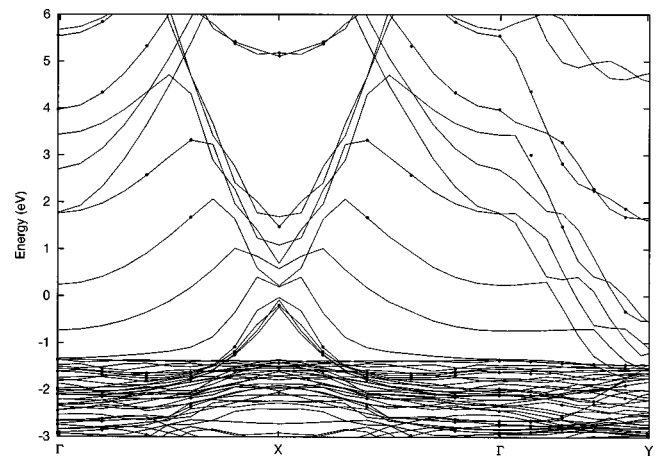


FIG. 2. Energy bands of the Cu(110) slab of 11 atomic plus 6 vacuum layers. The dots indicate surface electronic states determined by the criterion described in the text.

DOS. We can analyze these effects further by comparing the l projected partial DOS per atom for the innermost (*bulk*) and outermost (*surface*) layer of the slab also plotted in Fig. 1, lower panel. We focus on the d component, that is the dominant component to the total DOS. Here we see that there are some differences in the partial DOS among atoms in the bulk and surface layers. The main effect of the surface amounts to a depletion of d states at low energy in favor of the same states closer to E_F . The new states introduced by the surface in the DOS “tail” (see upper panel) have essentially d symmetry.

For the analysis of the optical properties it is important to know if surface states are formed. We can adopt a widespread quantitative criterion²¹ as a definition of an electronic surface state. This criterion states that: an electronic state is a surface state (s) or a bulk state (b) according to whether or not its total localization on the two outermost layers of the symmetric surfaces of the slab is larger than a given threshold $T > 4/11$ ($1/11$ being the localization of an equally distributed state in a slab of 11 layers). We have chosen a rather low threshold value, $T = 0.5$, in order to include at least all the states considered as surface states in photoemission experiments.^{6,22} In Fig. 2 we have plotted the energy bands of the slab indicating, by dots, surface states designed in this way. It can be seen that most of them form bands in the bulk “gaps,” as found also in previous calculations, whereas some isolated surface states are found among occupied bulk states. This division into s and b states will be used for the analysis of the surface optical properties in the next sections.

III. DIELECTRIC FUNCTION AND OPTICAL PROPERTIES OF THE (110) SURFACE

The optical properties of bulk Cu and of Cu(110) can be deduced from the dielectric tensor. This reduces to a single diagonal component $\epsilon^b(\omega)$ in the bulk and to three diagonal components $\epsilon^{[110]}$, $\epsilon^{[001]}$, and ϵ^\perp along the directions of the unit-cell basis vectors, respectively, for the slab geometry described above [ϵ^\perp refers to the direction perpendicular to

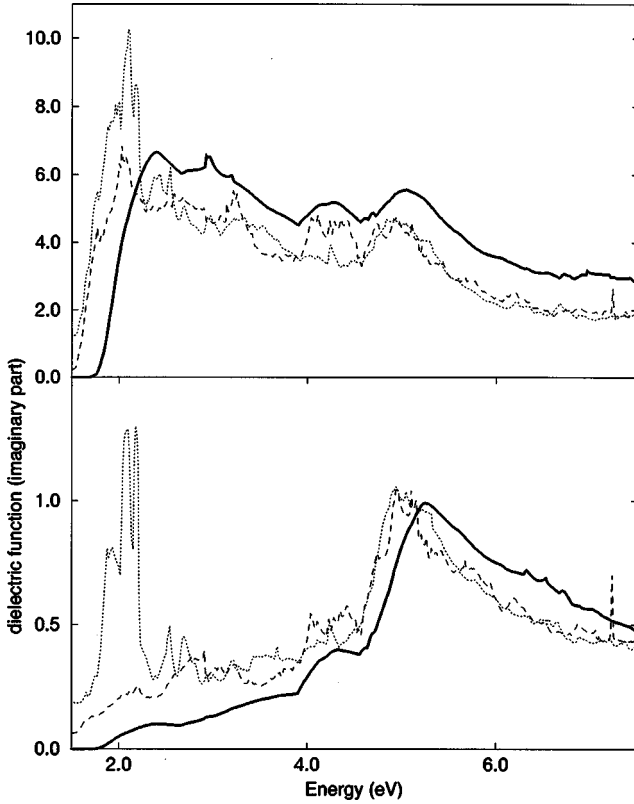


FIG. 3. Upper panel: imaginary part of the interband dielectric function $\epsilon_2^{[1\bar{1}0]}$ (dotted) and $\epsilon_2^{[001]}$ (dashed) for the Cu (110) slab and of ϵ_2^b (solid) in the bulk. Lower panel: the corresponding quantities from the interstitial region only (see text) are shown with the same symbols.

the (110) surface]. In metals, the dielectric function is determined by interband transitions, as in semiconductors, and intraband transitions stemming from excitations at low energy (the so-called Drude tail). The imaginary part of the interband dielectric tensor components may be computed *ab initio* as matrix elements of the momentum operator \mathbf{P} among wave functions of occupied and unoccupied states in different bands, according to the random-phase approximation.^{23,24} The real part of the dielectric function is then obtained by a Kramers-Kronig transform.

For the bulk case one can thus write (D stays for Drude, i for interband)

$$\epsilon(\omega) = (\epsilon_1^D + \epsilon_1^i) + i(\epsilon_2^D + \epsilon_2^i), \quad (3)$$

where the subscripts 1,2 in the above equation denote the real and imaginary parts of the dielectric function and the ω dependence in the right-hand side is understood. The Drude contribution is given by $\epsilon_1^D + i\epsilon_2^D = 1 - \omega_D^2/\omega(\omega + i\gamma)$, with the values of ω_D and γ quoted in Ref. 4. It has been shown⁴ that it is a good approximation to use the same formula, with the same Drude parameters, for the three components of the dielectric tensor in the slab.

In the upper panel of Fig. 3 we plot the imaginary part of the interband surface dielectric functions $\epsilon_2^{[1\bar{1}0]}$, $\epsilon_2^{[001]}$ (ϵ^{\perp}

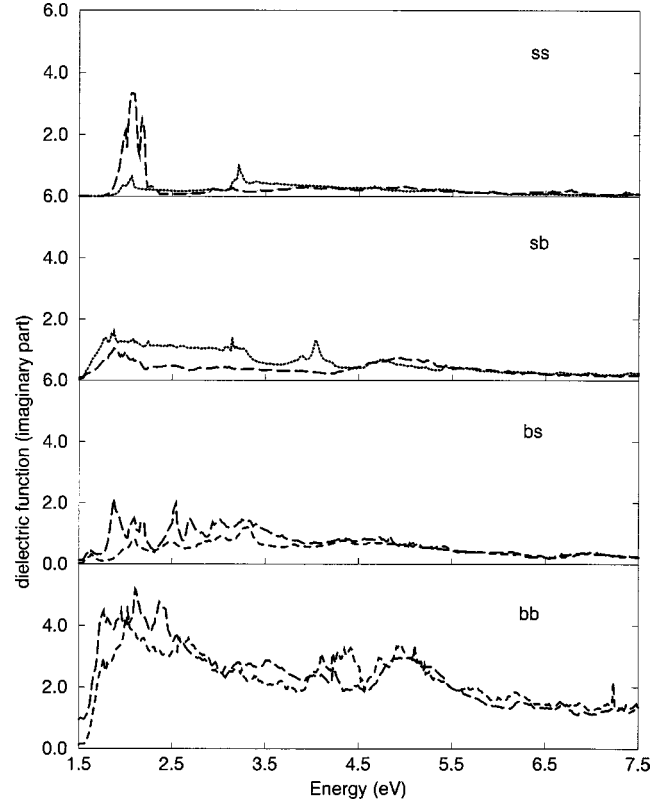


FIG. 4. Imaginary part of the slab interband dielectric function $\epsilon_2^{[1\bar{1}0]}$ (dashed) and $\epsilon_2^{[001]}$ (dotted) resolved into the contributions from the possible types of optical transitions: bulk-to-bulk states (bb), bulk-to-surface states (bs), surface-to-bulk states (sb), and surface-to-surface states (ss).

being irrelevant for the present analysis), and of the bulk ϵ_2^b for comparison. We have also plotted in the lower panel the contribution to the dielectric function components coming only from the interstitial part of the muffin-tin orbitals. This picture shows that the largest differences, ascribable to the surface, occur below 2.5 eV, where $\text{Im}[\epsilon_b^i(\omega)]$ drops to zero, whereas $\epsilon_2^{[1\bar{1}0]}$ and $\epsilon_2^{[001]}$ yield large structures. The ϵ 's show relevant differences just at energies where the RAS peaks are observed.^{4,6} Worth noting is that also the interstitial dielectric functions for the two directions are quite different with a peak at ≈ 2 eV in $\epsilon_2^{[1\bar{1}0]}$.

In order to investigate this point closer we have analyzed the optical matrix elements labeling the states as surface (s) or bulk (b) according to the criterion explained in the preceding section. Thus all matrix elements are divided into bulk-to-bulk, surface-to-surface, bulk-to-surface, and surface-to-bulk state transitions. These four different contributions to $\epsilon_2^{[1\bar{1}0]}$ and $\epsilon_2^{[001]}$ are plotted in Fig. 4. This plot confirms that the peaks occurring at low energy in the dielectric functions of the slab are indeed due to transitions among surface states, which are seen as weak structures in the range from -1 to 1.5 eV in the slab DOS of Fig. 1. This conclusion is important for a clearcut interpretation⁴ of spectra obtained by reflectance anisotropy^{6,9} experiments.

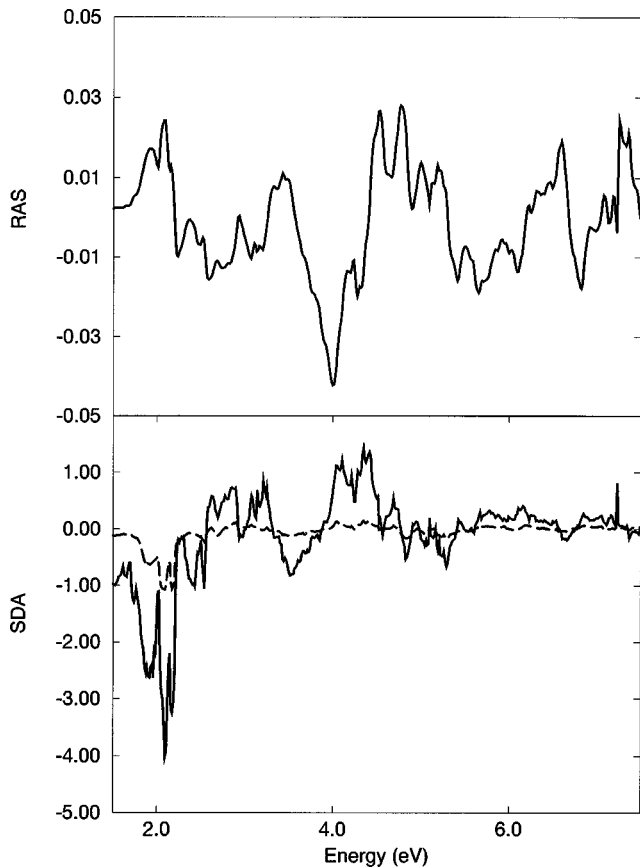


FIG. 5. Upper panel: calculated RAS for Cu (110). Lower panel: Imaginary part of the total SDA (solid) and without the interstitial contribution (dashed).

IV. SURFACE DIELECTRIC ANISOTROPY AND REFLECTANCE ANISOTROPY SPECTRUM

A RA experiment is still the most effective technique to get a fingerprint of the surface of a given metal. However, its effectiveness for applications depends on how detailed information on the morphologic and electronic structure of the interface can be extracted from the spectra. In a very recent paper⁴ we solved the problem of interpreting, by *ab initio* techniques, the RAS measured at Ag (Refs. 1,6) and Cu (Ref. 6) (110) surfaces. Presently, we perform calculations as described in the preceding sections. Our RAS for Cu (110) is calculated according to Eq. (1). The quantities $\Delta\epsilon_2$ and $\Delta\epsilon_1$, i.e., the imaginary and real part of the SDA, respectively, contain, in principle, an interband and an intraband term, according to Eq. (2). The anisotropic intraband part of the SDA has been estimated recently⁴ to have very small effects on the RA and we shall henceforth deal only with the interband term of the SDA. We plot in Fig. 5 the calculated RAS (upper panel), and $\Delta\epsilon_2$ (SDA) (lower panel) together with its part coming from the MT spheres only. The two characteristic features at ≈ 2 eV and between 4 and 5 eV in our plots are observed experimentally.⁶ Other structures appearing in the calculated RAS spectrum are washed out by a larger broadening in the experiment. In Ref. 4 we have discussed in detail the comparison between the calculated RAS and the experiments of Ref. 6. Our calculated bulk-induced structures

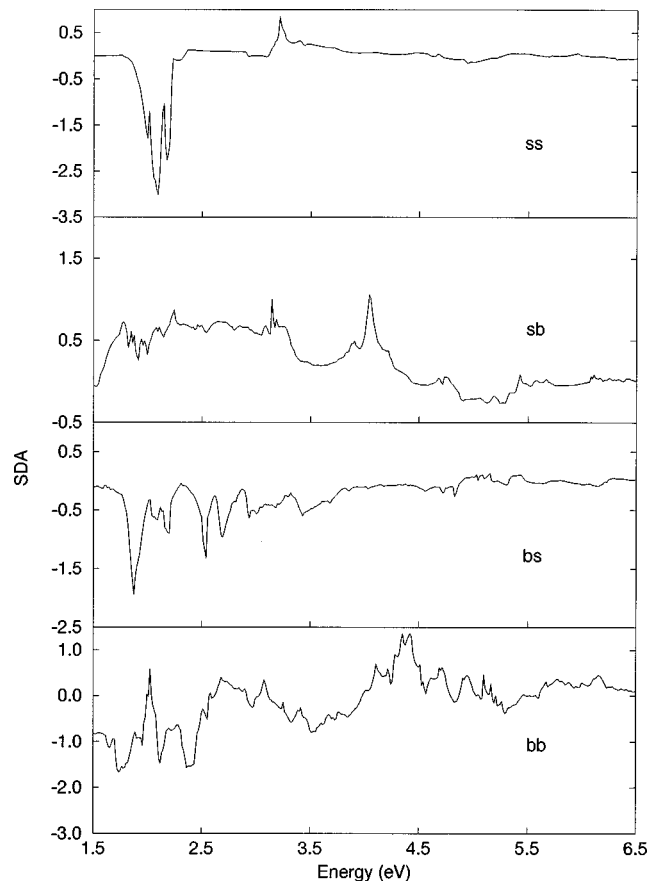


FIG. 6. Calculated SDA resolved into the contributions from the possible types of optical transitions: bulk-to-bulk states (bb), bulk-to-surface states (bs), surface-to-bulk states (sb), and surface-to-surface states (ss).

at 4 and 4.6 eV underestimate by 0.2 eV the corresponding experimental energies,⁴ as a consequence of neglecting self-energy corrections, which are in the range of 0.3–0.5 eV in Cu.^{25,26} Our smaller discrepancy, with respect to these values, is probably due to the different numerical/convergence accuracy of our calculations and to the slab geometry. As far as the peak close to 2 eV is concerned, we get almost perfect agreement with the experimental energy; this is probably due to the fact that self-energy corrections decrease with decreasing transition energies, as verified also for the Cu (100) surface electronic structure.²⁷

As pointed out very clearly in Ref. 4, $\Delta\epsilon$ in Eq. (1) embodies only the bare effect of the electronic transitions. The bulk dielectric function, in the denominator of Eq. (1), determines largely the final form of the RAS. In particular, the Drude term in ϵ^b reverses the negative peak in the SDA into the positive one in the RAS [see Eq. (1) and Fig. 5]. It is therefore very important to disentangle the intrinsic properties of the interface from Eq. (1). To this end we plot the SDA calculated separately for the four possible interband transitions: bulk-to-bulk states (bb), bulk-to-surface states (bs), surface-to bulk states (sb) and surface-to-surface states (ss), as displayed in Fig. 6. From this it is very clear that surface and bulk transitions contribute differently to the total SDA (and RAS) of Fig. 6. (We remind that these plots in-

clude both MTS and interstitial region contributions.) One sees that the peak at low energy must be definitely attributed to surface states, whereas the broader feature between 4 and 5 eV has mixed origin, while its large intensity in the RAS is due to the vanishing of the denominator in Eq. (1), namely to a bulk effect. This is at variance with the interpretation of Ref. 6 in terms of transitions from a surface state to a surface resonance. However, the distinction between a final bulk state (our interpretation) and a final surface resonance (see Ref. 6) is somehow arbitrary.

We now turn to the spatial analysis of the slab dielectric function, as anticipated in the Introduction. We have implemented the code to separate the dielectric function into the contributions of each atomic layer. More precisely, we carry out a layer by layer calculation of the integral in Eq. (2), neglecting nonlocality. (Namely, the contributions to the integral stemming from z and z' in different layers are neglected in this analysis: We have checked the accuracy of this approximation by showing that the slab ϵ , including nonlocal contributions, is very close to that given by the sum of the single-layer ϵ 's, not including nonlocal contributions.) Each atomic layer includes one atom (in the present case) centered on the corresponding MT sphere surrounded by the interstitial region. The vacuum layers, although physically distinct from the so-called interstitial region, are computationally treated as part of the interstitial region. We stress that, in our FP-LMTO code, the MT contributions to SDA may be resolved layer by layer, whereas this is not possible for the interstitial part that includes also the vacuum.

With this in mind, one can answer the question: where, in the slab, the SDA arises. As discussed briefly previously, the slab thickness had to be increased to 21 layers, to prevent any interaction of the innermost layer with the surface one. The individual contributions to $\Delta\epsilon_2$ were calculated for all atomic layers in the slab. There are altogether 11 nonequivalent layers out of the 21, the difference arising from the different positions with respect to the surfaces. In Fig. 7 the four panels from top to bottom show the SDA for the surface layer, the subsurface one, the fifth layer, and the central layer, respectively. The curves shown represent only the MT sphere contribution to the dielectric function anisotropy. One can see that (i) the SDA of the central layer (bulk like) is practically vanishing, as expected; (ii) the two main SDA structures, the ss peak below 2 eV, and the structure close to 3.5 eV, due to transitions involving also bulk states (see Fig. 6) are strongly present only at the surface layer underlying the vacuum. The subsurface layer, underlying the surface one, shows still some anisotropy in the SDA, whereas the fifth layer is practically isotropic as the bulk layer.

In view of the large interstitial contribution that can be deduced from the lower panel of Fig. 5, and of the vanishing anisotropy below the surface layer, we conclude that most of the anisotropy originates in the vacuum and in the surface layer. This of course does not discard the contribution of bulk states to the relevant transitions, since bulk states are present also in these regions.

V. CONCLUSIONS

The present calculations yield the *ab initio* determination of electronic and dielectric properties of a real metallic sur-

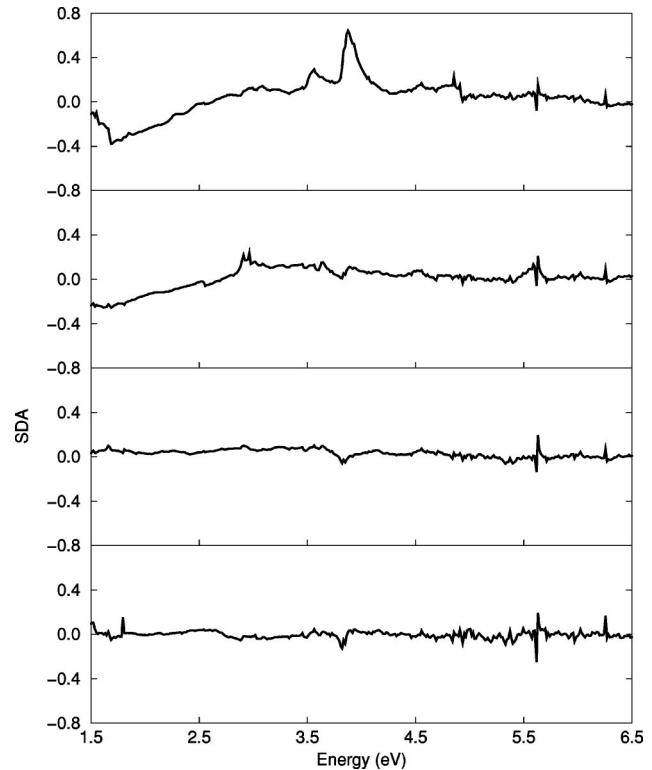


FIG. 7. Calculated SDA for four different types of atomic layers in the 21-layer slab (see text). From bottom to top: central layer (bulk like), fifth layer, layer just below the surface, surface layer. Only the MT sphere contribution is considered in each case.

face, including the reflectance anisotropy spectrum (RAS) and the surface dielectric anisotropy (SDA), opening the possibility of direct comparison with optical and energy-loss experiments.

Our RAS and SDA (Ref. 4) spectra for the Cu (110) surface are in satisfactory agreement with the experiments.⁶ Moreover, we are able to interpret the optical features according to two basically different criteria: (i) the surface or bulk character of the states involved in the relevant optical transitions (see Figs. 4 and 6), (ii) the SDA localization in real space (see Fig. 7). These two kinds of theoretical analyses provide, in practice, the scanning of the interface, from surface to bulk, with the resolution of one atomic layer. The relevance of this theoretical tool of investigation to the analysis of the interfaces of layered materials is obvious.

In particular we find that the SDA of the (110) surface of Cu mostly arises from the vacuum region and from the first atomic layer. It is almost completely absent in the middle layers, as expected, and weak in the subsurface layers. However, only the low-energy peak, below 2 eV, is due to transitions across surface states. The SDA features at higher energy are instead of predominant bulk-to-bulk, bulk-to-surface origin. According to our results, all these transitions are localized in the vacuum region and in the surface layer, where bulk states are also present. The RAS line shape, on the other hand, is strongly affected by a bulk effect, namely by $\epsilon_b - 1$ in the denominator of Eq. (1): not only does it yield a positive RAS close 2 eV, where the SDA is negative, but it

also strongly amplifies the RAS below 4 eV, where the denominator vanishes.

The effect of the surface relaxation upon the RAS, a “signature of the actual surface,” has been investigated carefully. We have calculated the RAS for two different relaxations (in the range 8–11% for the contraction of the distance between the first two outermost layers) and found that the one adopted by us gives a spectrum barely distinguishable from the other and only a little blueshifted with respect to the unrelaxed surface. Therefore the agreement of our RAS with the experimental one can be considered a sound and reliable result.

In conclusion, we have devised a theoretical *ab initio* method for the electronic and morphological analysis of surfaces and interfaces of real metals. In the case of Cu(110) we have disentangled surface and bulk effects in the RAS, analyzed the SDA (a surface effect) in terms of transitions in-

volving surface and/or bulk states, and found that its spatial localization is in the vacuum region and in the first atomic layer. These results are, in our opinion, of great importance for interpreting experimental data as well as for predicting optical properties in new layered material, surfaces with adsorbates²⁸ and so on. We hope that the present work will stimulate new measurements in the field of surface optical properties of metals.

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