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Optical anisotropy of $YBa_2Cu_3O_{7-x}$

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The optical anisotropy of $YBa_2Cu_3O_{7-x}$ in the 0.08–5.6 eV region is investigated by polarized reflectance measurements on single crystals, and by transmittance, reflectance, and ellipsometric measurements on oriented thin films. In the visible–near-uv spectral region the anisotropy is relatively mild, but a huge anisotropy is observed in the infrared. Here, the reflectance increases with decreasing frequency for *both* polarizations, consistent with metallic conductance both parallel and perpendicular to the *ab* plane. The *c*-axis plasma frequency is strikingly low, but there is strong damping which could originate from a continuum of low-energy interband transitions.

$YBa_2Cu_3O_{7-x}$ (Y-Ba-Cu-O) and related high-T_c cuprates are currently the subject of intensive research worldwide.[1,2] One of the major issues is the effective dimensionality of these materials, which can be addressed in principle from the anisotropy of their electronic properties. With this objective, the conductance anisotropy of Y-Ba-Cu-O single crystals has been studied by several groups,[3,4] who reported values of $\rho_\perp/\rho_\parallel$ between 30 and 200. However, extrinsic effects such as planar stacking faults, microcracks, inhomogeneous oxygen concentration, etc., may be a serious problem in single crystals and could well affect the dc results. In principle, high-frequency ac conductance and optical measurements are less subject to ambiguities of these sorts, because charge displacements are rather small in such experiments. However, no conclusive results have been reported yet. Some indirect information has been inferred from apparent discrepancies between single-crystal[5,6] and bulk-ceramic[7] reflectance data, which have been resolved,[6,8] based on analogy with La_2NiO_4, by *postulating* Y-Ba-Cu-O (as well as $La_{2-x}Sr_xCuO_4$) to be highly anisotropic—in fact, metallic in the *ab* plane and insulating in the *c*-axis direction.

Here, we present optical data which show that, although Y-Ba-Cu-O is indeed highly anisotropic in the infrared region, the *c*-axis polarized reflectance is not characteristic of insulating material but rather shows a metalliclike rise with decreasing photon energy.

Single crystals of Y-Ba-Cu-O were grown at Princeton University by the flux method in an oxygen flow. The average size of the crystals was $0.5\times0.5\times0.1$ mm^3 and they had shiny faces of high optical quality and sharply defined edges. Typical T_c's were between 91 and 93 K, with 0.5-K wide transitions. To measure the resistivity by the Montgomery technique, 25-μm Au wires were indium-soldered onto the largest crystal faces near the corners.

Thin Y-Ba-Cu-O films were deposited on $SrTiO_3$ substrates by reactive magnetron sputtering[9,10] at Stanford University. Thicknesses ranged from 500 Å to 1 μm. The quality of the films can be judged from their low normal-state resistivities, sharp (1–2 K wide) superconducting transitions, and high critical current densities of up to 1.2×10^7 A/cm^2 at 4.2 K. X-ray diffractograms of these films showed a high degree of epitaxial orientation. Some of the films were grown with the *c* axis and others with the *a* axis (predominantly) perpendicular to the (001) face of the substrate.

Mid-ir reflectance spectra of the single crystals were obtained with a Digilab FTS-40 Fourier-transform infrared (FTIR) spectrometer coupled to a Spectratech IR-PLAN microscope that provided spatial resolution of 50 μm. This allowed us to record polarized ir reflectance spectra not only from the large platelet faces which are parallel to the *ab* plane, but also from the platelet sides which are perpendicular to the *ab* plane. We changed the polarization by rotating the Zn-Se polarizer or by rotating the sample; the results were consistent in both cases as can be seen from spectra D and E in Fig. 1.

As no instrumentation available to us could achieve sufficient spatial resolution to measure the optical spectra of the platelet sides at higher photon energies, we supplemented these results with near-ir, visible, and near-uv data obtained from transmittance, reflectance, and ellipsometric measurements on oriented thin films. In addition to the FTIR spectrometer, we used a near-ir-visible-near-uv Perkin-Elmer Lambda-9 double-monochromator double-beam spectrophotometer and a near-ir-visible-near-uv spectroellipsometer.[11]

For a normal-incidence measurement on a film with a typical grain orientation of ~80%, one has $\mathbf{E}\perp\mathbf{c}$ in ~60% of the grains in *a*-axis-oriented films, as compared to ~90% in *c*-axis-oriented ones, for either polarized or unpolarized light. Although ellipsometry is a non-normal-incidence technique, the pseudodielectric response $\langle\epsilon\rangle$ (that calculated from the ellipsometric data in the two-phase model without regard to anisotropy or surface

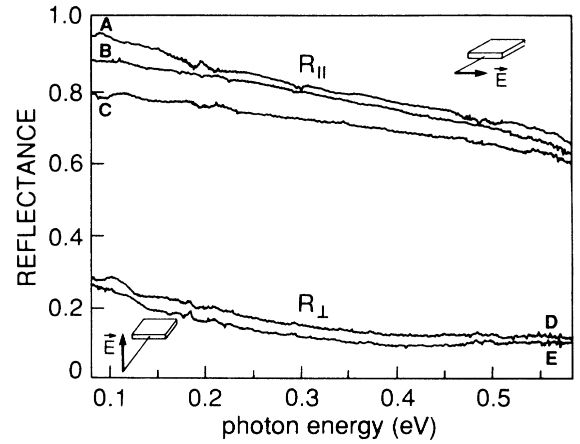

FIG. 1. Polarized infrared reflectance of Y-Ba-Cu-O, at normal incidence, from (A) single crystal, *ab* face; (B, D, E) single crystal, side perpendicular to *ab* face; (C) *c*-axis-oriented film (pristine surface). The $R_{\perp}(\omega)$ spectra were obtained by rotating for 90° the polarizer (D) or the crystal (E). The reflectance of films was raised to that of (A) when the surface was cleaned by ion milling the top 500–1000 Å.

effects) can give a fairly accurate measure, under certain conditions and for properly aligned samples, of the individual principal components of the dielectric tensor of a uniaxial medium.[12] Using the orientation statistics of these films, we estimate that Fig. 2(a) (in the whole energy range) and Fig. 2(b) (above 2.5 eV) yield $|\epsilon_{\parallel}|$ and $|\epsilon_{\perp}|$, respectively, to within 20%.

Since many physical parameters of Y-Ba-Cu-O depend very sensitively on preparation, impurities, defects, etc. (which accounts for many conflicting reports), at this stage we prefer to use large sample sets. Hence, we recorded altogether about 50 reflectance spectra from various faces of four single crystals, ellipsometric spectra from about two dozen thin films, and transmittance and reflectance spectra from a few hundred films.

Typical normal incidence ir reflectance spectra from a "side"—i.e., a face perpendicular to the *ab* plane—of a Y-Ba-Cu-O single crystal are shown in Fig. 1 for light polarized parallel and perpendicular to the CuO_2 layers. A large anisotropy is apparent. The actual anisotropy may be even larger because of possible artifacts due to surface imperfections, sample misalignment, incomplete light polarization, etc. However, the high metallic $R_{\parallel}(\omega)$ shown in curve B does not differ by more than a few percent from the reflectance spectra of the large platelet faces which are parallel to the *ab* plane (curve A) or from those of our other single crystals and our best *c*-axis oriented films (curve C).

The real and the imaginary parts of the pseudodielectric function $\langle\epsilon(\omega)\rangle=\epsilon_1(\omega)+i\epsilon_2(\omega)$, determined from ellipsometric measurements, are shown in Figs. 2(a) and 2(b) for a *c*-axis- and an *a*-axis-oriented thin Y-Ba-Cu-O film, respectively. (Note that these films are not as dense as Y-Ba-Cu-O single crystals, which indeed show[13] somewhat larger ϵ_1 and ϵ_2.) The overall similarity of the two sets of spectra is clearly apparent, with the major differences being in the occurrence and position of spectral features above 3 eV and in the appearance of a free-electronlike component in the *c*-axis data below about 2.5 eV. This low-energy feature is also seen in data taken on the *ab* faces of single crystals.

To cast these data in the form more directly suitable for comparison to the reflectance data of Fig. 1, we have used them to calculate the corresponding reflectance spectra and have also plotted the results in Fig. 3. The measured reflectance of a *c*-axis-oriented film (the dashed curve)

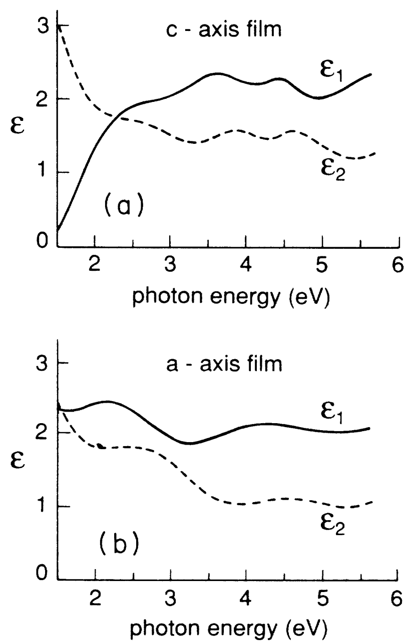

FIG. 2. The complex pseudodielectric functions $\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)$ of (a) *c*-axis oriented thin Y-Ba-Cu-O film, and (b) *a*-axis-oriented film, of comparable density.

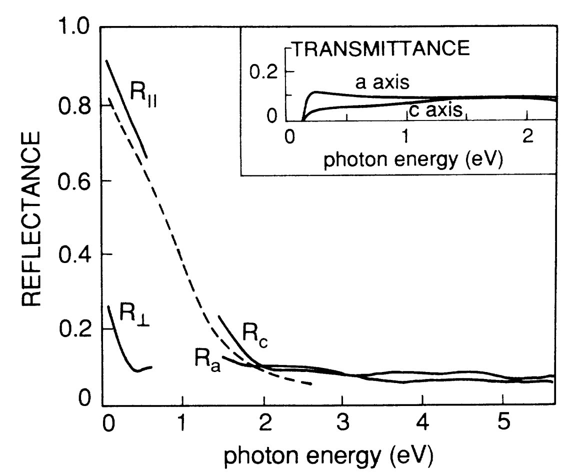

FIG. 3. Reflectance (from Fig. 1) of Y-Ba-Cu-O single crystal, $R_{\parallel}$ and $R_{\perp}$, compared to that of thin films, R_c and R_a [broken curve: measured; solid curve: calculated from Fig. 2]. Note that R_a has a component of $R_{\parallel}$. Inset: Transmittance of ~2000-Å-thick Y-Ba-Cu-O films, on $SrTiO_3$ substrates, oriented with *c* axis and *a* axis perpendicular to the substrate. The cutoff is due to the substrate absorption.

and the transmitances of both c-axis- and a-axis-oriented films (the inset) are shown in Fig. 3. Consistency among the three experimental techniques utilized is apparent and, in fact, is further improved when the differences in the degree of orientation are taken into account. The anisotropy is seen to be very large in the ir region and to decrease with increasing photon energy, diminishing to relatively small values in the visible and near-uv regions. These spectra, and hence the anisotropy, do not change much[14] with temperature down to 77 K, i.e., well below the superconducting transition, in the $0.15 < \hbar\omega < 3$-eV spectral range.

Let us turn now to the question of effective dimensionality. Of principal interest here are the low-frequency single-crystal polarized-reflectance data of Fig. 1. Notice first that $R_\perp(\omega)$ actually also shows a metalliclike upturn at frequencies below ~ 0.4 eV or so; this is even more apparent in Fig. 3. It does not appear insulatinglike in any event, in contrast to tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ), hexamethyltetraselenafulvalene tetracyanoquinodimethane (HMTSF-TCNQ), or $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ and similar low-dimensional materials where $R_\perp(\omega)$ remains low and nearly constant down to the phonon-frequency region. Hence Y-Ba-Cu-O, although certainly strongly anisotropic, does not look like a quasi-two-dimensional metal on the basis of its optical properties. Furthermore, some consistency among different experimental data can be achieved within the present description.

We use the least-squares fit to the simple Drude model, $\epsilon(\omega) = \epsilon(\infty) - \omega_p^2/\omega(\omega + i\Gamma)$, and get $\hbar\omega_p^\perp \approx 0.7$ eV, $\hbar\Gamma_\perp \approx 0.9$ eV, $\epsilon_\perp(\infty) \approx 4$. From these parameters and utilizing the relation $\rho = 4\pi\Gamma/\omega_p^2$, one gets $\rho_\perp \approx 10$ mΩ cm. Since $\rho_\parallel = 250$–400 $\mu\Omega$ cm, this amounts to $\rho_\perp/\rho_\parallel = 25$–$40$, in reasonable agreement with dc conductance experiments.[15] Notice, however, that the above values of $\omega_p^\perp$ and $\Gamma_\perp$ are quite uncommon to ordinary metals: The plasma frequency is more than order-of-magnitude too low while the damping is anomalously strong. Another important parameter is the optical effective mass, $m_\perp^*$. From $\omega_p^2 = 4\pi ne^2/m^*$ and assuming the carrier density $n \approx 6\times 10^{21}$ cm^{-3} (which has been suggested from the Hall effect measurements[3,10]) one gets $m_\perp^* \approx 15 m_e$, which certainly is uncommon.

As for the low-frequency "heavy-axis" plasmons —which play the central role in some theoretical models of high-T_c superconductivity—it seems that in Y-Ba-Cu-O they are too strongly damped to be well-defined excitations of the system. In fact, we expect two or more bands to cross the Fermi level[16] in Y-Ba-Cu-O. In that case, there should be a continuum of optically allowed (i.e., "vertical") low-energy interband transitions. That could well be related to the observed "strong damping of free carriers." A continuum of electronic transitions, featureless and nearly flat (at room temperature) should show up also in Raman scattering, and indeed it was observed[14] in dozens of good superconducting Y-Ba-Cu-O thin films (from the lowest Raman shifts detectable all the way up to 1 eV), as well as in single crystals.[17] It would be interesting to see what is happening in other high-T_c superconductors not isostructural with Y-Ba-Cu-O, i.e., the cuprates containing La, Bi, and Tl.

Finally, our $R_\perp(\omega)$ does come with an error bar, as pointed out above; also, it would be desirable to extend the single-crystal reflectance anisotropy data further into far infrared. From the present reflectance data, we cannot rule out the existence of a very small gap, of ~ 50 meV or so, for the conduction in the c-axis direction. If that were the case, one would expect $R_\perp(\omega)$ to show a strong temperature dependence.[18]

In conclusion, we have presented optical data (polarized reflectance spectra from different faces of single crystals, and transmittance, reflectance, and ellipsometric spectra of oriented thin films), which show that Y-Ba-Cu-O is not very anisotropic in the visible/near-uv region, but that it is rather anisotropic in the midinfrared and below. However, the reflectance with light polarization perpendicular to the CuO_2 layers rises at low frequencies, as expected from metallic rather than insulating behavior. In the range of frequencies investigated here, no evidence is found for the *qualitatively* distinct in-plane and out-of-plane transport mechanisms. The data are consistent with existence of a continuum of low-energy interband transitions. Given the important theoretical implications of this issue, extension of the spectroscopical measurements to the lower frequencies and to other related cuprate materials is important and is underway.

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[15] Actually, $\rho_\perp$ was observed to increase with decreasing temperature in Refs. 3. However, Iye *et al.* (Ref. 4) found that both $\rho_\parallel$ and $\rho_\perp$ show metallic behavior in some Y-Ba-Cu-O single crystals—reportedly those which showed sharper superconducting transitions. A similar finding was reported also by S. Hagen *et al.*, at the American Physical Society Meeting, New Orleans, 1988 (unpublished).

[16] Indeed, in Y-Ba-Cu-O two CuO_2 layers traverse the unit cell and one expects that a pair of $3d_{x^2-y^2}/2p_x(2p_y)$ bands should be close and nearly parallel to one another throughout the Brillouin zone.

[17] S. L. Cooper *et al.*, Phys. Rev. B **37**, 5290 (1988).

[18] None of the (over a dozen) optical studies on polycrystalline samples published so far by several groups showed more than a few percent change in reflectance, for $0.03 < \hbar\omega < 3$ eV, when the temperature was lowered from 300 down to 10 K. However, a recent study on Y-Ba-Cu-O single crystals [A. G. Thomas *et al.* (unpublished)] reports a substantial decrease of $R_\parallel(\omega)$, for $\hbar\omega < 0.15$ eV, at low temperatures.