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c-axis infrared response of $Tl_2Ba_2Ca_2Cu_3O_{10}$ studied by oblique-incidence polarized-reflectivity measurements

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We show that from measurements of the reflectivity of a uniaxial medium taken at a finite incidence angle with s- and p-polarized light it is possible to determine the dielectric function both parallel and perpendicular to the optical axis. When applied to layered compounds with its surface parallel to the layers, this technique allows for an accurate determination of the loss function perpendicular to the layers. This is demonstrated for the example of c-axis-oriented thin films of the high-T_c superconductor $Tl_2Ba_2Ca_2Cu_3O_{10}$, on which we carried out polarized reflectivity measurements at 45° incidence angle above and below T_c.

I. INTRODUCTION

One of the remarkable properties of the cuprate high-T_c superconductors, apart from their extremely high transition temperatures, is the anisotropy of their electronic properties, such as dc resistivity, optical conductivity, magnetic penetration depth, etc. Such anisotropy is indeed expected from their layered crystal structures. In most cases a direct study of the optical anisotropy requires preparation of single-crystal samples since various crystal faces and axes need to be accessed. Such an analysis has been carried out with normal-incidence infrared reflectometry for $La_{2-x}Sr_xCuO_4$,[1] $YBa_2Cu_3O_{7-\delta}$,[2,3] $Pb_2Sr_2DyCu_3O_8$,[4] and $Bi_2Sr_2CaCu_2O_8$.[5] Although larger single crystals gradually become available for this kind of study, it is useful to have an experimental technique for determining the dielectric function along the c axis for those materials of which thin films or thin single-crystal platelets exist, but of which no thick single crystals are available. Also it may serve as a second complementary approach since, for example, in epitaxially grown thin films it is often easier to obtain a homogeneous oxygen distribution than in single crystals.

In this paper we introduce an experimental technique based upon the reflectivity measurements at oblique incidence angles with two different polarizations of the light. Using Kramers-Kronig relations for the experimentally measured $R_s(\omega)$ and $R_p(\omega)$ (the reflectivity measured with s- and p-polarized light, respectively), it is possible to calculate the tensor components $\epsilon_{ab}(\omega)$ and $\epsilon_c(\omega)$ of the complex dielectric function for the directions parallel and perpendicular to the ab plane, respectively. We demonstrate both theoretically and experimentally that indeed this method gives reasonable results for the energy loss function along the c axis even if only the ab faces of the crystal are available for reflectivity measurements. As an example we study a c-axis-oriented epitaxial thin film of the high-T_c superconductor $Tl_2Ba_2Ca_2Cu_3O_{10}$, for which single crystals were synthesized only recently and the typical c-axis dimension of the plateletlike crystals is again much smaller than 1 mm. Hence most optical studies of this material were limited to the ab-plane response and only a glimpse of the c-axis response was present in early studies of ceramic samples.[6] Although it has been shown that the optical anisotropy of thin platelets of $YBa_2Cu_3O_{7-\delta}$ (Ref. 7) and $Bi_2Sr_2CaCu_2O_8$ (Ref. 8) can be determined with an infrared microscope with the light beam focused to a very small region (typically 200 μm) on the ac face, the operational wavelengths were diffraction-limited to the midinfrared region. Such limitations do not occur if oblique-incidence-angle reflection spectroscopy of the much larger ab face is employed.

II. OUTLINE OF THE METHOD

The complex reflection coefficients for a uniaxial crystal, with its optical axis oriented perpendicular to the surface of reflection, are given by the expressions[9–11]

$$r_s = \frac{\cos\theta - \sqrt{n_o^2 - \sin^2\theta}}{\cos\theta + \sqrt{n_o^2 - \sin^2\theta}},$$
$$r_p = \frac{n_o n_e \cos\theta - \sqrt{n_e^2 - \sin^2\theta}}{n_o n_e \cos\theta + \sqrt{n_e^2 - \sin^2\theta}} \tag{1}$$

for s- and p-polarized light, respectively. Here θ is the incidence angle and n_o and n_e are the complex refractive indices for the ordinary and extraordinary rays, respectively.

Experimentally one has to determine the reflected *intensities* $R(\omega)$ for a wide range of frequencies. Hence, one has $r^2 = Re^{2i\phi}$ of which only R is measured experimentally, while the phase ϕ is calculated from R using the Kramers-Kronig relations. For s-polarized light the usual convention is to have ϕ restricted to the interval from 0 to π. Due to experimental uncertainties negative values of ϕ may arise, leading to spurious negative values of the real part of the ab-plane optical conductivity $\sigma_{ab}(\omega)$ which one obtains by inverting the expression for r_s. For p-polarized light the situation is different, as even in the absence of experimental errors the phase may become negative.

Once the coefficients r_s and r_p are known the indices n_o and n_e, or the corresponding complex dielectric functions ϵ_o and ϵ_e can be found by solving Eq. (1) for them in terms of r_s and r_p:

$$\epsilon_o = \sin^2\theta + \cos^2\theta\left(\frac{1-r_s}{1+r_s}\right)^2 ,$$
$$\epsilon_e = \sin^2\theta\left[1-\epsilon_o\cos^2\theta\left(\frac{1-r_p}{1+r_p}\right)^2\right]^{-1} . \qquad (2)$$

Given ϵ_o and ϵ_e, it is possible to derive all other key spectral functions such as optical conductivity and loss functions.

Our new method can be applied directly to reflectivity measurements on c-axis-oriented high-T_c superconducting thin films (we assume a tetragonal crystal structure). The quantities with subscript o (for "ordinary") then correspond to the in-plane (the ab plane) parameters and those with subscript e (for "extraordinary") correspond to the axial (the c axis) parameters. As for these materials the conduction parallel to the ab plane is known to be metallic, with an almost insulating or semiconducting behavior along the c axis, we can derive an approximate expression of the reflectivity for p-polarized light when the sample surface corresponds to the ab plane. Let us first introduce the parameters $l \equiv (\cos\theta)^{-1}\sqrt{1-\epsilon_c^{-1}\sin^2\theta}$ and $x = n_{ab}^{-1}$, with the help of which we can write the corresponding absorptivity for the p-polarized light in the form

$$1 - R_p = 4\frac{\mathrm{Re}(x\cdot l^*)}{|1+x\cdot l^*|^2} .$$

As $\mathrm{Im}n_{ab} \gg 1$ in the limit of metallic conductivity along the ab plane, we can use $1/\mathrm{Im}n_{ab}$ as the expansion parameter of a Taylor series. Furthermore we make an expansion for $|\sin^2\theta/\epsilon_c| \ll 1$, so that the leading term of the series expansion is given by

$$1 - R_p = \frac{2\sin^2\theta}{\mathrm{Im}n_{ab}\cos\theta}\mathrm{Im}\left(-\frac{1}{\epsilon_c}\right) . \qquad (3)$$

We see that, for a smoothly varying n_{ab}, the absorptivity of p-polarized light has peaks which are essentially the peaks in the loss function along the c axis. The physical mechanism behind this type of resonance is in fact similar to that underlying the Berreman effect[12] for dielectric overlayers on metallic substrates. Although we will use the full inversion formulas of Eq. (2), Eq. (3) already shows that the c-axis loss function obtained from such an inversion is less prone to experimental errors than, *e.g.*, the c-axis conductivity.

III. EXPERIMENT

With this motivation, we have undertaken a study of optical anisotropy in $Tl_2Ba_2Ca_2Cu_3O_{10}$, for which high-quality large-area c-axis-oriented thin films are available. Our superconducting c-axis-oriented $Tl_2Ba_2Ca_2Cu_3O_{10}$ thin films were grown by sputter deposition at ambient temperature in a symmetrical rf diode sputtering system from two identical 1/2 in. targets. The films are typically 5000 Å thick and have critical temperatures in the range 120–123 K. The details of film growth techniques and sample characterizations were published elsewhere.[13]

Our oblique-incidence reflectivity measurements were carried out in a Bruker 113v Fourier Transform Infrared Spectrometer (FTIR) with a CryoVac variable-temperature exchange-gas cryostat. The infrared spectra were acquired at temperatures of 108, 163, and 300 K. The samples and the reference Au mirrors were mounted together inside the cryostat for calibration of reflectivity at each temperature during the measurement.

IV. RESULTS AND DISCUSSIONS

In Fig. 1 we present the reflectivity spectra for s- and p-polarization at various temperatures. As expected, the reflectivity R_s for s-polarized light is higher than the reflectivity R_p for p-polarized light throughout the frequency and temperature range of our measurement. The R_s spectra of $Tl_2Ba_2Ca_2Cu_3O_{10}$ are quite representative of the ab-plane response of high-T_c superconductors in general. The more or less featureless, quasilinear frequency dependence is quite evident.

A marked difference between our R_s and R_p spectra is the existence of strong absorption features positioned at 400 and 620 cm^{-1} due to the excitation of c-axis longitudinal optical phonons. This assignment is supported by the absence of these fairly strong features in the R_s spectra. Furthermore, from the reflectivity spectra of ceramic $Tl_2Ba_2Ca_2Cu_3O_{10}$ samples[6] where a number of c-axis longitudinal optical phonons clearly appear in the infrared range, one can easily identify the two phonon peaks positioned near 400 and 620 cm^{-1}, respectively. The lattice dynamics calculation for $Tl_2Ba_2Ca_2Cu_3O_{10}$ by Kulkarni *et al.*[14] also predicts two c-axis longitudinal optical phonons in the vicinity of these features. According to the above authors, there are A_{2u} longitudinal optical modes situated at 421 and 616 cm^{-1}. The former corresponds to the vibration along the c axis of the oxygen atoms in the CuO_2 and BaO planes against the Ca atoms. The latter corresponds to the vibration along the c axis of the oxygen atoms in the BaO planes and the

Ca atoms against the oxygen atoms in the central CuO_2 planes.

In Fig. 2 we display the c-axis loss function of $Tl_2Ba_2Ca_2Cu_3O_{10}$ at various temperatures. We can easily recognize the two corresponding features due to

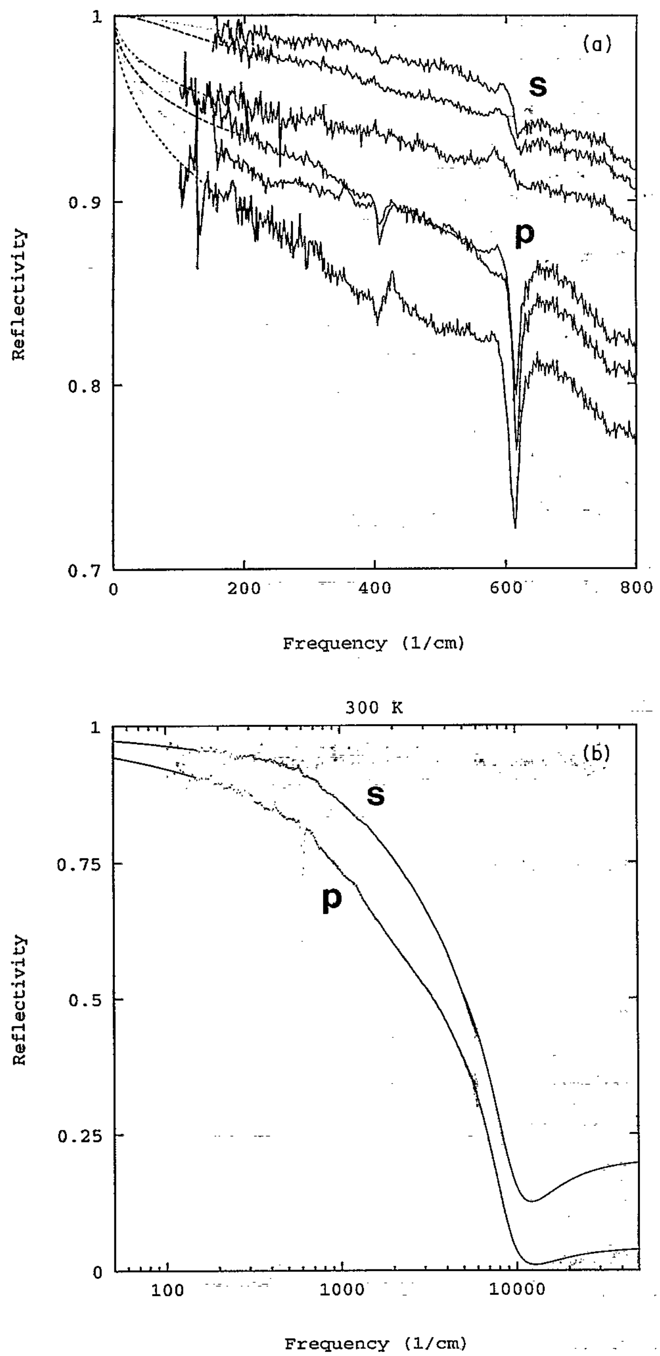

FIG. 1. (a) Reflectivity of $Tl_2Ba_2Ca_2Cu_3O_{10}$ for s-polarized light (the top three curves) and p-polarized light (the bottom three curves), measured at 45° angle of incidence. The temperatures are 108, 163, and 300 K from top to bottom for each set of three curves. (b) Room temperature reflectivity (dots) measured with s-polarized (top) and p-polarized (bottom) and high- and low-frequency extrapolations used for the Kramers-Kronig analysis (solid curves) above 6000 cm^{-1} and below 100 cm^{-1}.

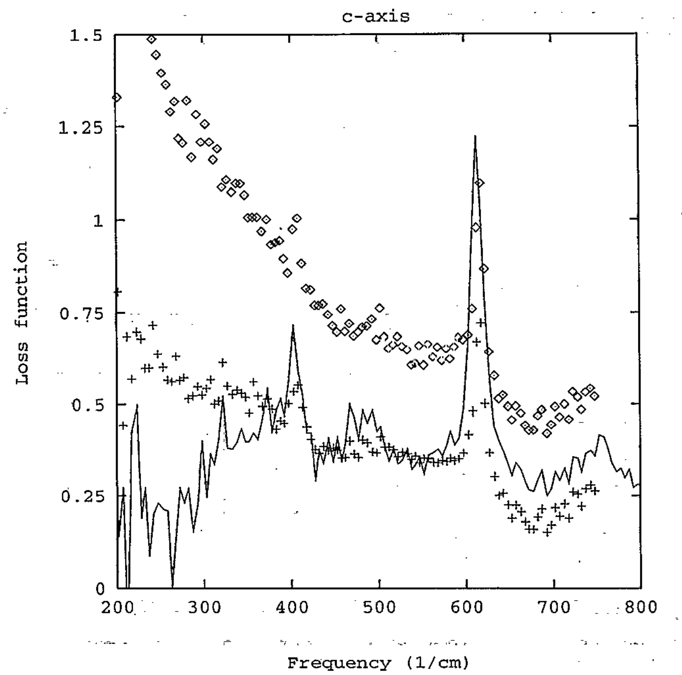

FIG. 2. The loss function for $\mathbf{E} \parallel \mathbf{c}$. The temperatures are 108 (lozenges), 163 (crosses), and 300 K (solid curve).

the aforementioned c-axis longitudinal optical phonons. These phonon modes do exhibit some change with temperature. Both the 400 cm^{-1} and 620 cm^{-1} shift to higher frequencies by about 5 cm^{-1} as the temperature changes from 300 K to 108 K.

The electronic background in the c-axis loss function is more or less flat at room temperature and the 163 K spectrum is not much different from the 300 K case. However, in the case of 108 K (below T_c), there is a rise in the electronic-background intensity in the low-frequency region. This can be interpreted as the high-frequency tail of the loss function peak due to the formation of the c-axis optical plasmon of the superconducting electrons. Based on this observation, we place an upper limit of 200 cm^{-1} or 25 meV on the c-axis plasmon energy.

Let us compare our findings with the experimental reports on other high-T_c superconductors. Even though all of $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_8$, and $Tl_2Ba_2Ca_2Cu_3O_{10}$ have an in-plane optical plasmon at about 1 eV,[15] the energy of the c-axis plasmons varies from one system to another. In the case of $YBa_2Cu_3O_{7-\delta}$ there is a zero crossing of ϵ_c at around 100 cm^{-1}, i.e., below the lowest transverse optical mode, corresponding to a longitudinal mode of mixed vibrational and electronic character.[2] At higher temperatures this zero crossing shifts to lower frequencies and eventually disappears, apparently due to an enhanced damping. A similar behavior has been observed in $La_{2-x}Sr_xCuO_4$,[1] where the lowest longitudinal out-of-plane mode is found at 30 cm^{-1}. $Bi_2Sr_2CaCu_2O_8$ (Ref. 5) does not show any trace of an out-of-plane plasmon either at room temperature or well below T_c even down to 30 cm^{-1}, which is then taken as an experimentally determined upper limit.

Band structure calculations based on the local density approximation (LDA) can be used to determine intra-

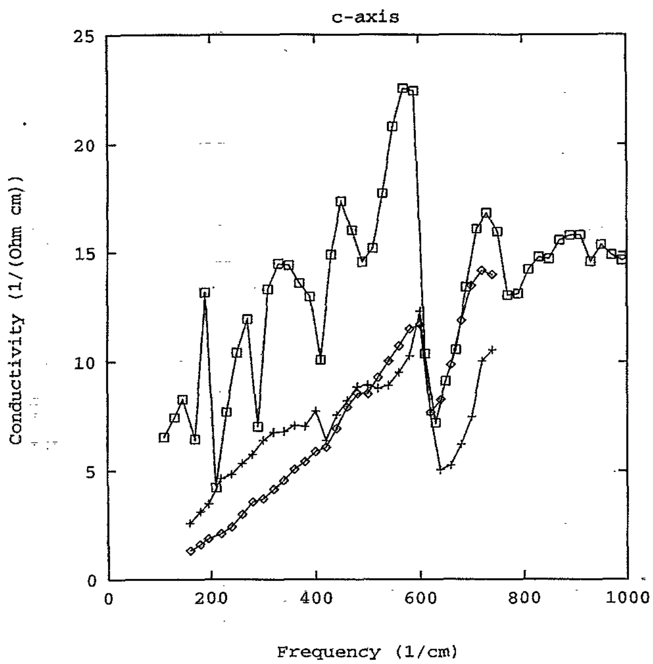

FIG. 3. The conductivity for **E** ∥ **c**, for 108 K (lozenges), 163 K (crosses), and 300 K (squares).

and interband plasmon frequencies. Calculations for $Bi_2Sr_2CaCu_2O_8$ were done by Uspenskii and Rashkeev,[16] who obtained bare plasma frequencies of 3.3 and 0.9 eV for **E** ⊥ **c** and **E** ∥ **c**, respectively, and about 1.5 eV for the screened in-plane plasmon. The calculation of Maksimov *et al.* for $YBa_2Cu_3O_{7-\delta}$ gives unscreened intraband plasma frequencies (determined from a properly weighted Fermi velocity) of 3.5, 4.2, and 1.05 eV for **E** parallel to the *a*, *b*, and *c* directions,[17] respectively, which should be scaled with a factor of 0.5 to obtain the screened plasma frequencies ($\omega_p^{scr} = \omega_p/\sqrt{\epsilon_\infty}$, with $\epsilon_\infty \approx 4$). For $La_{2-x}Sr_xCuO_4$ the LDA results for the screened in-plane and out-of-plane plasmons are 1.9 eV and 0.4 eV, respectively.[18,19]

So we see that the experimental value of the in-plane plasmons of optimally doped samples is about half the value of the LDA calculation. For the out-of-plane plasmon this discrepancy is even more dramatic, and the overestimation of LDA amounts to one or more orders of magnitude. This is in accordance with the notion of confinement due to incoherent interlayer hopping, as was proposed by Anderson.[20]

In Fig. 3 we display the *c*-axis conductivity for our $Tl_2Ba_2Ca_2Cu_3O_{10}$ sample at various temperatures. As we mentioned previously the *c*-axis conductivity is more susceptible to errors than the *c*-axis loss function. However, one can say that below T_c there is a tendency of depression in the *c*-axis conductivity below 600 cm^{-1}. We can compare our results with the *c*-axis conductivity of $YBa_2Cu_3O_{7-\delta}$ above and below T_c determined from reflection measurements on the *ac* face of single crystals by Bauer[2] and Homes *et al.*[3] According to these authors, there is a gaplike depression of conductivity at low temperatures below 600 cm^{-1}, but there is no clear evidence of a true BCS-like gap. Hence the situation for $YBa_2Cu_3O_{7-\delta}$ is quite similar to what we found in our own investigation of $Tl_2Ba_2Ca_2Cu_3O_{10}$.

V. CONCLUSION

We demonstrate the feasibility of an experimental technique to obtain the dielectric function in the directions parallel and perpendicular to the optical axis of a uniaxial sample, by oblique-incidence polarized reflectometry. We applied this technique to a thin film of $Tl_2Ba_2Ca_2Cu_3O_{10}$ in order to study the *c*-axis infrared response. For this material no single crystals are available which are sufficiently elongated along the *c* axis to allow a direct scattering experiment on the *ac* face. Although the longitudinal optical phonons in the *c* axis are clearly present, no plasma-related zero crossing of ϵ_c is found above 200 cm^{-1}, which indicates that 200 cm^{-1} is an upper limit for the out-of-plane plasmon.

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