In-plane polarized collective modes in detwinned YBa$_2$Cu$_3$O$_{6.95}$ observed by spectral ellipsometry

C. Bernhard$^1$, T. Holden$^1$, J. Humlíček$^2$, D. Munzar$^2$, A. Golnik$^3$, M. Kläser$^4$, Th. Wolf$^4$, L. Carr$^5$, C. Homes$^5$, B. Keimer$^1$, and M. Cardona$^1$

1) Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany.

2) Institute of Condensed Matter Physics, Masaryk University, Kotlářská 2, CZ-61137 Brno, Czech Republic.

3) Institute of Experimental Physics, Warsaw University, Hoża 69, 00-681 Warsaw, Poland.

4) Forschungszentrum Karlsruhe, ITP, D-76021 Karlsruhe, Germany.

5) National Synchrotron Light Source, Brookhaven National Laboratory, USA.

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Abstract

The in-plane dielectric response of detwinned YBa$_2$Cu$_3$O$_{6.95}$ has been studied by far-infrared ellipsometry. A surprisingly large number of in-plane polarized modes are observed. Some of them correspond to pure phonon modes. Others possess a large electronic contribution which strongly increases in the superconducting state. The free carrier response and the collective modes exhibit a pronounced a-b anisotropy. We discuss our results in terms of a CDW state in the 1-d CuO chains and induced charge density fluctuations within the 2-d CuO$_2$ planes.

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The far-infrared (FIR) dielectric response of the cuprate high-T_c superconductors (HTSC) has been extensively studied by conventional reflection and absorption techniques [1–7]. Nevertheless, some important aspects of the FIR in-plane response remain unsettled, such as the low-energy electronic excitations in the superconducting (SC) state or the in-plane polarized IR-active phonon modes. The accuracy of the most popular reflectance technique is limited by the reference problem (the absolute value of the reflectivity, R, is required) and by the need of a Kramers-Kronig analysis which involves extrapolation of R towards zero and infinite frequency. Both problems become particularly important if R is close to unity such as for the FIR in-plane response of HTSC. In this manuscript we present experimental data of the in-plane dielectric response of a detwinned YBa$_2$Cu$_3$O$_{6.95}$ single crystal which have been obtained by spectral ellipsometry. This technique has the advantage that it is self-normalizing and allows one to measure directly the complex dielectric function, $\tilde{\varepsilon}=\varepsilon_1+i\cdot\varepsilon_2$ [8]. We find that the in-plane dielectric response contains a surprisingly large number of collective modes, some of which posses an unusually large spectral weight (SW) and exhibit pronounced anomalies at the SC transition. These modes thus seem to involve collective excitations of the charge carriers and of the SC condensate. The observed in-plane anisotropy of the electronic background and the collective modes cannot be consistently explained in terms of a superposition of independent contributions from CuO$_2$ planes and 1-d metallic CuO chains. Our results rather suggest that the 1-d CuO chains enhance (or possibly even induce) a charge density modulation within the 2-d CuO$_2$ planes.

The ellipsometric measurements were performed at the U4IR and U10A beamlines of the National Synchrotron Light Source (NSLS) in Brookhaven, USA. We used a homebuilt setup attached to a conventional Fourier spectrometer [9,10]. The high brilliance of the synchrotron allows us to study small crystals in grazing incidence geometry ($\varphi=85^\circ \pm 1^\circ$) which is required for metallic samples with a Brewster-angle close to $90^\circ$ [10]. Since the dielectric response of HTSC is strongly anisotropic we performed measurements for different configurations of the principal axis (a, b, and c) with respect to the plane of incidence of the light. The tensor components of $\tilde{\varepsilon}$ have then been obtained by standard numerical procedures [8]. We have
previously shown by measurements on gold films that a meaningful determination of $\tilde{\epsilon}$ for millimeter size metallic samples requires to take diffraction effects into account \[10\]. One of us (J.H.) has studied these effects theoretically for a sample with infinite conductivity and has developed an inversion procedure \[11\] which we have successfully applied to data on small gold films \[10\]. The same procedure was used for the present data.

A Y-123 single crystal of size $2.8 \times 4 \times 0.6$ mm$^3$ ($a \times b \times c$) was flux-grown in an Y-stabilized ZrO$_2$ crucible. It was annealed for one week in flowing oxygen at 420 °C resulting in $T_c=91.5(\pm0.8)$ K as determined by dc-SQUID magnetometry. One ab- and one ac-face were polished to optical grade before the crystal was mechanically detwinned as confirmed by inspection under a polarizing optical microscope. Micro-Raman measurements confirm the detwinning and the high quality of the surface \[12\]. They also reveal a strong SC induced anomaly of the $B_{1g}$ mode at 340 cm$^{-1}$ which is characteristic for slightly overdoped Y-123 \[13\].

Figures 1(i) and 1(ii) display the real part of the a-axis optical conductivity, $\sigma_{1,a}(\nu)$, and of the dielectric function, $\epsilon_{1,a}(\nu)$ at 100 and 10 K (thin and thick solid lines). The broad electronic features are similar to those reported for reflectivity data \[1,2,5-7\]. The NS the conductivity consists of a Drude-like peak at low frequencies that merges with a broad MIR-band which extends beyond the displayed range. In the SC state a pronounced dip appears in $\sigma_{1,a}(\nu)$ with an onset around 950 cm$^{-1}$ and a sharp minimum around 320 cm$^{-1}$. For $\nu>1000$ cm$^{-1}$ (inset of Fig 1(i)), $\sigma_{1,a}$ does not change between 100 and 10 K. This signals that the redistribution of electronic spectral weight (SW) associated with the formation of the SC condensate involves an energy scale of around 1000 cm$^{-1}$. Notably, a sizeable Drude-like peak persists even in the SC state at 10 K. Its signature was observed also in the reflection and absorption data \[2,3,5-7\], by microwave measurements \[14\] and by mm-wave spectroscopy \[15\]. Evidently, a significant fraction of quasiparticles (QP) does not participate in the macroscopically coherent and thus loss-free response of the SC condensate which is represented in $\sigma_1$ by a delta peak at zero frequency ($\sigma_1 \sim \nu_{p,SC}^2 \delta(\nu)$), and in
\(\varepsilon_1\) by a term \((\varepsilon_1 \approx -\nu_{p,SC}^2/\nu^2)\), where \(\nu_{p,SC}^2\) is the plasma frequency of the condensate. Two kinds of processes can be expected to contribute to a finite low-frequency conductivity. Firstly, scattering of charge carriers on structural or magnetic defects leads to pair-breaking and thus gives rise to unpaired QP’s. This process should be very efficient for the cuprate HTSC with their d-wave SC order parameter \([16]\). Secondly, dephasing processes of the SC condensate can also give rise to a finite conductivity at non-zero frequency. They can arise for example due to a spatial variation of \(n_s\) such as has recently been proposed based on THz-spectroscopy measurements on Bi-2212 \([17]\).

In our ellipsometric spectra we also observe a number of well defined modes. Our result for the SW, \(S=(\pi^2 \cdot c \cdot \varepsilon_o \cdot \nu_o^2)^{-1} \int \sigma(\nu) d\nu\), the resonance frequency (RF), \(\nu_o\), and the half-width at half-maximum, \(\Gamma\), as obtained from fits with a Lorentzian function, is listed in table I. The modes at 280, 360, and 600 cm\(^{-1}\) have been previously identified \([2,7]\) and have been assigned to phonon modes. The observation that these modes have a similar SW as in the insulating parent compound YBa\(_2\)Cu\(_3\)O\(_6\) \([18,19]\) has been interpreted in terms of a surprisingly poor screening by the charge carriers of the CuO\(_2\) planes which may be related to an inhomogeneous charge distribution \([7]\). In addition to these phonons we observe two more modes at 230 and 190 cm\(^{-1}\) which exhibit a remarkable behavior. Their RF’s are close to the ones of some in-plane polarized phonon modes in YBa\(_2\)Cu\(_3\)O\(_6\) (see table I). For both modes, however, the SW becomes extraordinarily large in the SC state; at 10 K it exceeds the one of the pure phonon mode by more than an order of magnitude. The SW of a phonon mode is, \(S=(4\pi/V_c) [\sum_k e_k^* \xi_k]^2/|\sum_k m_k \cdot \xi_k^2 \cdot v_o^2|\), where \(V_c\) is the unit cell volume, \(e_k^*\) and \(m_k\) are the dynamic charge and the mass of the ion \(k\) and \(\xi_k\) its relative direct displacement. If the two present modes were to be interpreted as pure phonons, their huge SW would imply that they involve dynamic charges far in excess of the ones of the bare ions. They can thus be rather ascribed to collective electronic excitations. The drastic SW increase below \(T_c\) furthermore suggests that they correspond to excitations of the SC condensate. Above \(T_c\) they are hardly detectable and possibly correspond to the pure phonon modes. The eigenvectors of the IR phonon modes in Y-123 have been previously obtained from lattice dynamical calculations.
One a-polarized mode near 200 cm$^{-1}$ involves the in-plane motion of O(2) and Cu(2) against O(3) and thus will couple mainly to charge density oscillations within the CuO$_2$ planes. The other relevant mode near 170 cm$^{-1}$ involves predominantly the motion of O(1) against Cu(1) and therefore is sensitive to charge density oscillations within the CuO chains.

We point out that our ellipsometric data provide sound evidence for the low-energy modes. The spectra show the true dielectric function which is corrected for anisotropy. The diffraction corrections are smooth functions of d/λ where d is the sample dimension in the plane of incidence and λ is the wavelength and thus cannot result in any sharp features. Also, ellipsometry measures the real- and the imaginary parts of $\tilde{\varepsilon}$ independently. This allows us to check the KK-consistency of the spectral features and thus to distinguish them from structures related to noise or imperfections of the setup. It is also very unlikely that the KK-consistent modes are caused by a damaged surface layer. This conclusion is supported by our micro-Raman data which are even more sensitive to the surface layer quality.

Irrespective of their large SW, the signature of these modes is rather weak in the normal incidence reflectivity, R, such as displayed in the inset of Fig. 1(ii). Nevertheless, they seem to appear in some published spectra. In particular, they have been identified in an earlier absorptivity measurement.

Figures 2(i) and 2(ii) display the spectra of $\sigma_{1,b}(\omega)$ and $\varepsilon_{1,b}(\omega)$ at 100 and 10 K (thin and thick solid lines). The broad electronic response again agrees fairly well with the previously reported one. In particular, a sizeable anisotropy is evident between the a- and the b-axis response with $\sigma_{1,b}(\nu)/\sigma_{1,a}(\nu) \sim 2$ in the NS, and $n^b_a/n^a_a=(\lambda_a/\lambda_b)^2 \approx (1700\text{ Å}/1200\text{ Å})^2 \sim 2$ in the SC state, with the SC magnetic penetration depth, $\lambda_{a,b}$, derived from $\lambda_{a,b}^{-1}=\lim_{\nu\to 0}\left\{\sqrt{4\cdot \pi^2 \cdot \nu^2 \cdot (1 - \varepsilon_{1,a,b}(\nu))}\right\}$ (spectra are not shown). The enhanced free carrier response along the b-axis direction was previously explained in terms of the fully oxygenated 1-d CuO chains which are thought to be metallic and to become SC due to proximity effect. Our spectra also reveal a large anisotropy of the energy scale of the SC condensation process, i.e., of the range over which $\sigma_1(\nu)$ is reduced below its value at $T_c$. In the b-axis spectrum this energy scale is significantly larger (it exceeds the measured range).
than in the a-axis one. A similar trend appears in some reflectivity data \cite{5,6}. Such a large anisotropy of the energy scale of the SC condensation process is hardly consistent with the scenario of a proximity induced SC state in the CuO chains which should lead to a decrease of the energy scale rather than to the apparent increase.

Our b-axis spectra contain a surprisingly large number of collective modes. At least nine modes are resolved in the 10 K spectrum at 140, 190, 230, 260, 295, 340, 360, 480 and 560 cm$^{-1}$. Furthermore, the modes at 230, 290 and 480 cm$^{-1}$ exhibit a doublet structure. Table II lists the obtained values for $S$, $\nu_o$, and $\Gamma$. Only the modes at 360 and 560 cm$^{-1}$ have a SW consistent with the assignment to pure phonon modes. The large SW of the modes at 140, 190, 230, 260, 295, 340 and 480 cm$^{-1}$ suggests again that they involve electronic degrees of freedom. Interestingly, these modes preserve a sizeable SW even in the NS, unlike the two a-axis ones which almost disappear above $T_c$. For orthorhombic YBa$_2$Cu$_3$O$_7$ group theory predicts seven IR-active phonon modes for both a- and b-polarization \cite{20}. The multitude of the observed b-polarized modes thus is indicative of an enlarged unit cell or a reduced symmetry along the b-direction. It is well known that 1-d metals are susceptible to structural and electronic instabilities, such as a transition to a dimerized state or a charge density wave state (CDW) \cite{21}. Indeed, recent NQR- and STM measurements indicate that the CuO chains of YBa$_2$Cu$_3$O$_7$ are in a CDW state \cite{22,23}. They furthermore suggest that the CuO chains interact with the CuO$_2$ planes and enhance (or possibly even induce) a charge density modulation therein in the SC state \cite{22}. Such a scenario is consistent with our observation of a-axis electronic modes which develop in the SC state and a large number of b-axis polarized ones which occur already in the NS. The scenario of a CDW state within the CuO chains, however, contradicts the explanation of the in-plane anisotropy of the electronic conductivity in terms of metallic CuO chains. A CDW is easily pinned by impurities, the CuO chains consequently should be only poorly conductive. A broad hump around 250 cm$^{-1}$ which is very pronounced in the 10 K spectrum may well be associated with localized charge carriers of the CuO chains. A similar feature has previously been observed along the chain direction in Y-123 \cite{2} and Y-124 \cite{4}. The apparent contradiction can be resolved if...
one associates the a-b-plane anisotropy of the free carrier response with the CuO$_2$ planes themselves. Given that charge density fluctuations are intrinsic to the CuO$_2$ planes, the interaction with the CuO chains may indeed induce a strong anisotropy of the electronic response. The most prominent example is the so-called stripe phase model which assumes a pattern of alternating hole rich and hole poor 1-d stripes \[23\]. Within such a scenario it is feasible that the interaction with the CuO chains causes the stripes to become aligned along the b-direction, some experimental evidence is reported in Ref. \[24\]. Such an arrangement could indeed account for the observed anisotropy of the conductivity. However, it would lead to a reduced symmetry along the a-axis direction rather than along the b-axis one such as suggested by our experiments. Therefore, it seems that one has to consider both effects, a CDW state within the CuO chains and charge fluctuations within the CuO$_2$ planes that develop due to the interaction with the 1-d CuO chains. In this context it will be very interesting to learn whether similar collective modes and anisotropy effects can be observed in other high-T\(_c\) cuprates without 1-d CuO chains.

In summary, by ellipsometry we studied the in-plane FIR dielectric response of detwinned YBa$_2$Cu$_3$O$_{6.95}$. We observe a surprisingly large number of collective modes. Some of them correspond to in-plane polarized phonons such as observed in undoped YBa$_2$Cu$_3$O$_6$. Others have an unusually large spectral weight (SW) and therefore seem to involve collective excitations of the charge carriers, possibly even of the superconducting condensate. The collective modes and the free carrier response exhibit a pronounced a-b anisotropy. We discussed our results in terms of a CDW state in the 1-d CuO chains and induced charge density fluctuations within the 2-d CuO$_2$ planes.

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Table 1: Values of the fitting parameters for the a-axis modes at 10 K compared to the in-plane phonon modes of YBa$_2$Cu$_3$O$_6$ at 300 K from \[19\] and \[18\].
| S   | \( \nu_o \) (cm\(^{-1}\)) | \( \Gamma \) (cm\(^{-1}\)) | S\(^a/b\) | \( \nu_o^{a/b} \) (cm\(^{-1}\)) | \( \Gamma^{a/b} \) (cm\(^{-1}\)) |
|-----|----------------|----------------|---------|----------------|----------------|
| 0.7(0.04) | 595.6(0.2) | 25.1(0.6) | 0.6/0.4 | 588/595 | 26/28 |
| 1.55(0.03) | 362.3(0.1) | 6.8(0.3) | 1.55/2.5 | 357/351 | 30/34 |
| 2.3(0.2) | 279.4(0.4) | 41.2(2.2) | 0.85/1.4 | 231/246 | 14/8 |
| 53.8(1.2) | 228.2(1.8) | 59.8(5.1) | 0.75/1.9 | 193/188 | 10/11 |
| 18.5(0.5) | 189.5(0.1) | 10.2(0.8) | 1.05/2.1 | 118/116 | 9/8 |

Table 2: Values of the fitting parameters for the b-axis modes.

| T=100K | T=10K |
|--------|-------|
| S \( \nu_o \) (cm\(^{-1}\)) | \( \Gamma \) (cm\(^{-1}\)) | S \( \nu_o \) (cm\(^{-1}\)) | \( \Gamma \) (cm\(^{-1}\)) |
| 2.28(0.11) | 545.3(0.56) | 28.3(1.2) | 3.8(0.1) | 544.9(0.4) | 36(2) |
| 11.5(0.4) | 480.8(0.28) | 53.4(2.5) | 13.6(0.3) | 476.8(0.2) | 46.6(1.3) |
| 1.3(0.3) | 362.9(0.3) | 12.1(0.8) | 1.25(0.1) | 362.1(0.3) | 8.1(0.2) |
| 2.5(0.2) | 343.3(0.2) | 6.8(0.5) | 4.4(0.2) | 343.8(0.2) | 8.2(0.2) |
| 8.3(0.7) | 302.4(0.2) | 20(fix) | 14.7(0.6) | 299.6(0.6) | 19.8(0.8) |
| 5.6(0.5) | 289.4(0.8) | 20(fix) | 15.1(0.9) | 287.0(0.7) | 21.3(1.0) |
| 3.2(0.3) | 285.6(0.7) | 12.1(1.7) | 5.8(0.5) | 261.9(0.7) | 16.7(0.8) |
| 10.5(0.9) | 238.8(0.9) | 20.2(2.1) | 48.9(2.6) | 236.1(1.0) | 29.6(2.9) |
| - | - | - | 41.4(2.1) | 220.1(0.7) | 24.1(3.2) |
| 22.5(1.2) | 192.1(0.4) | 13.8(2.2) | 23.9(1.1) | 189.0(0.2) | 8.2(0.9) |
| 15.4(1.4) | 174.6(0.8) | 13.4(1.7) | 124.0(5.2) | 139.3(2.3) | 43.9(8.5) |
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I. FIGURE CAPTIONS

Figure 1: a-axis component of the real part of (i) of the conductivity and (ii) of the dielectric function of YBa$_2$Cu$_3$O$_{6.95}$ ($T_c=91.5$ K) at 100 K (thin solid line) and 10 K (thick solid line). Arrows mark the collective modes. Inset: (i) $\sigma_{1a}(\nu)$ over an extended spectral range and (ii) normal incidence reflectivity, $R_a$, as deduced from the ellipsometric data.

Figure 2: b-axis component of the real part of (i) the far-infrared conductivity and (ii) of the dielectric function of YBa$_2$Cu$_3$O$_{6.95}$ ($T_c=91.5$ K) at 100 K (thin solid line) and 10 K (thick solid line). Dotted (solid) arrows mark the collective (doublet) modes. Inset: (i) $\sigma_{1b}(\nu)$ over an extended spectral range and (ii) normal incidence reflectivity, $R_b$, as deduced from the ellipsometric data.
