The anomaly of the oxygen bond-bending mode at 320 cm\(^{-1}\) and the additional absorption peak in the c-axis infrared conductivity of underdoped YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) single crystals revisited by ellipsometric measurements

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Abstract

We have performed ellipsometric measurements of the far-infrared c-axis dielectric response of underdoped YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\) single crystals. Here we report a detailed analysis of the temperature-dependent renormalization of the oxygen bending phonon mode at 320 cm\(^{-1}\) and the formation of the additional absorption peak around 400-500 cm\(^{-1}\). For a strongly underdoped YBa\(_2\)Cu\(_3\)O\(_{6.5}\) crystal with \(T_c=52\) K we find that, in agreement with previous reports based on conventional reflection measurements, the gradual onset of both features occurs well above \(T_c\) at \(T^*\sim150\) K. Contrary to some of these reports, however, our data establish that the phonon anomaly and the
formation of the additional peak exhibit very pronounced and steep changes right at $T_c$. For a less underdoped YBa$_2$Cu$_3$O$_{6.75}$ crystal with $T_c=80$ K, the onset temperature of the phonon anomaly almost coincides with $T_c$. Also in contrast to some previous reports, we find for both crystals that a sizeable fraction of the spectral weight of the additional absorption peak cannot be accounted for by the spectral-weight loss of the phonon modes but instead arises from a redistribution of the electronic continuum. Our ellipsometric data are consistent with a model where the bilayer cuprate compounds are treated as a superlattice of intra- and inter-bilayer Josephson-junctions.

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I. INTRODUCTION

It was early recognized that some of the infrared active c-axis phonon modes of the high-\textit{T}_c cuprate superconductors (HTSC) exhibit rather strong changes (so-called ‘phonon anomalies’) in the vicinity of the superconducting transition \[1\]. The most pronounced phonon anomalies have been observed for those compounds which contain two (or three) closely spaced CuO\textsubscript{2} layers per unit cell, like the bilayer compounds YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7−δ} (Y-123) \[2,3\], YBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} (Y-124) \[4\] and Pb\textsubscript{2}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8} \[5\], or the trilayer system Tl\textsubscript{2}Ba\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{10} \[6\]. In Y-123 and Y-124 the most pronounced renormalization occurs for the so-called oxygen bond-bending mode at 320 cm\textsuperscript{-1} which involves the in-phase vibration of the O(2) and O(3) oxygen ions of the CuO\textsubscript{2} planes against the Y-ion which is located in the center of the bilayer and against the ions of the CuO chains \[7\]. The renormalization of the 320 cm\textsuperscript{-1} mode is accompanied by the formation of an additional broad absorption peak in the frequency range between 400 to 500 cm\textsuperscript{-1} at low temperature. The effects are most spectacular for strongly underdoped YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6.5−6.6} with \textit{T}_c \sim 50-60 K. Here the phonon mode at 320 cm\textsuperscript{-1} softens by almost 20 cm\textsuperscript{-1} and loses most of its spectral weight which is transferred to the additional broad peak. As the hole doping of the CuO\textsubscript{2} planes increases, the anomaly of the 320 cm\textsuperscript{-1} phonon mode becomes less pronounced. Simultaneously, the additional peak shifts towards higher frequencies and becomes considerably weaker.

Evidently, there exists an intimate relationship between the strong anomaly of the oxygen bond-bending mode at 320 cm\textsuperscript{-1} and the formation of the additional absorption peak. The underlying mechanism, however, is yet unknown and the subject of an ongoing discussion \[1,8,9\].

Recently van der Marel and coworkers have proposed a very interesting explanation for the additional absorption peak \[10,11\]. They assumed that the CuO\textsubscript{2} planes of underdoped HTSC are not coherently coupled, not even the closely spaced planes of the bilayers. From this point of view a bilayer superconductor like Y-123 can be treated as a stack of two-dimensional superconducting layers which forms a superlattice of intra- and inter-bilayer
Josephson-junctions. The dielectric response of such a superlattice of Josephson junctions exhibits two zero-crossings corresponding to two longitudinal Josephson-plasmons: the inter-bilayer and the intra-bilayer one. In addition, it has a pole corresponding to the so called ‘transverse optical Josephson plasmon’ [10]. Van der Marel have suggested that the additional absorption peak discussed above may correspond to this transversal resonance. Very recently they have confirmed their suggestion by more quantitative considerations regarding the doping dependence of the peak position [11]. Some of us have shown that this model can be extended to account not only for the presence of the additional peak but also for the related phonon anomalies [12]. The essential idea consists in including the local electrical fields acting on the ions that participate in the phonon modes. In particular, the model has allowed us to explain the details of the anomaly of the 320 cm$^{-1}$ phonon mode in Y-123. This has been shown to arise from a dramatic change of the local electrical field acting on the in-plane O(2)- and O(3)-ions caused by the onset of inter- and intra-bilayer Josephson effects.

The verification of the existence of intra-bilayer Josephson plasmons, may have rather far reaching consequences. The finding that even the closely-spaced CuO$_2$ layers are only weakly (i.e. Josephson) coupled along the c-axis would favor models which predict that the electronic ground state of the CuO$_2$ planes is unconventional, involving charge confinement to the planes and incoherent coupling between the planes in the normal state [13]. So far, the existence of the Josephson plasma resonance has been firmly established only for the case of CuO$_2$ planes (or pairs of planes) that are separated by insulating layers much wider than the in-plane lattice constant. Such examples are the studies of the c-axis transport [14,15], the microwave absorption [16] or the FIR c-axis conductivity [17–19]. Even two different longitudinal plasma modes have been recently observed in the T$^*$ phase SmLa$_{1-x}$Sr$_x$CuO$_4$ which has two kinds of blocking layers: the fluorite type Sm$_2$O$_2$ layers and the rocksalt-type (La,Sr)$_2$O$_2$ layers [20].

In order to establish the above interpretation of the anomalies in the c-axis conductivity of underdoped Y-123, two points have to be clarified which have not been discussed in our
previous communication [12]. Firstly, according to the model of the superlattice of inter- and intra-bilayer Josephson junctions (let’s call it a Josephson-superlattice-model) the phonon anomalies should become very pronounced only below $T_c$, while they can appear somewhat above $T_c$ for the strongly underdoped and most anisotropic samples as a result of pairing fluctuations within the bilayers. From the previous experimental results it was not clear whether this is the case. Reflectance measurements performed on strongly underdoped Y-123 single crystals rather seemed to indicate that the anomaly of the $320 \text{ cm}^{-1}$ phonon sets in well above $T_c$ at a temperature $T^* \gg T_c$ and proceeds without any noticeable change at $T_c$ [3, 9]. The temperature dependence of the phonon anomaly rather seemed to resemble [3, 21] that of the spin-lattice relaxation rate $(T_1 T)^{-1}$ or the Knight shift observed in NMR experiments, both of which are determined by the to the so-called ‘spin-gap phenomenon’, i.e., by a gradual and incomplete depletion of the low energy spin excitations. These speculations are supported by Zn substitution experiments: the Zn substitution is known to suppress the spin-gap effect [22] and it has also been shown to remove the anomaly of the $320 \text{ cm}^{-1}$ phonon mode and the additional absorption peak [1]. Second, the model predicts that the additional peak should acquire a considerable part of its spectral weight (SW) from the electronic background, to be more specific from the superconducting condensate [12]. This prediction is not consistent with Ref. [2] where it has been suggested that the SW of the additional peak is fully accounted for by the spectral-weight loss ($\Delta$SW) of the phonon modes at 320 and 560 cm$^{-1}$.

In the following we report an ellipsometric study of the far-infrared (FIR) c-axis dielectric response of two underdoped YBa$_2$Cu$_3$O$_{7-\delta}$ single crystal: one strongly underdoped ($\delta \approx 0.5$, $T_c=52$ K), the other moderately underdoped ($\delta \approx 0.25$, $T_c=80$ K). In particular, we present a detailed analysis of the anomaly of the oxygen bond-bending mode at $320 \text{ cm}^{-1}$ and of the additional absorption peak. In case of the strongly underdoped crystal our ellipsometric measurements establish that the temperature-evolution of the phonon anomaly and the additional absorption peak exhibits a two-step behavior with a smooth onset at $T^* \sim 150 \text{K} \gg T_c=52$ K followed by a sudden and steep change right at $T_c=52$ K. For the
For both crystals our data establish that the absorption peak obtains only some part of its spectral weight from the phonon system while a substantial part (at least 40-50%) arises from the electronic background.

II. EXPERIMENTAL TECHNIQUE

A. Sample preparation

The YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals with typical dimensions of 2x2x(0.5-1) mm$^3$ have been grown in Y-stabilized Zr$_2$O crucibles [23]. For the ellipsometric measurements we used only crystals with a smooth and shiny as-grown surface containing the c-axis. A strongly oxygen deficient crystal has been prepared by sealing it in an evacuated quartz tube together with a large amount of Y-123 powder whose oxygen content has been previously adjusted to $\delta \approx 0.5$ (by annealing in 0.1% O$_2$ in Ar at 530$^\circ$ C and subsequently quenching into liquid nitrogen). The quartz-ampule containing the crystal and the powder was annealed at 500 $^\circ$C for 10 days and subsequently slowly cooled to room temperature. A second, moderately underdoped YBa$_2$Cu$_3$O$_{6.75}$ crystal has been prepared by annealing in a flowing oxygen gas stream at 550 $^\circ$C and subsequent rapid quenching. The critical temperature $T_c$ and the transition width $\Delta T_c$ (10 to 90% of the diamagnetic shielding) have been determined by DC-magnetization measurement in zero-field-cooled (zfc) and field-cooled (fc) mode ($H_{ext}=$5 Oe) using a commercial SQUID magnetometer. Figure 1 shows the temperature-dependent volume susceptibility, $\kappa_V$, for the YBa$_2$Cu$_3$O$_{6.5}$ crystal with $T_c$=52 K and $\Delta T_c$=3 K (open circles) and the YBa$_2$Cu$_3$O$_{6.75}$ crystal with $T_c$=80 K and $\Delta T_c$=4 K (solid squares).

B. Technique of far-infrared ellipsometry

The quantity measured in ellipsometry [24] is the complex reflectance ratio
$$\tilde{\rho}(\omega, \Phi) = \frac{\tilde{r}_p(\omega, \Phi)}{\tilde{r}_s(\omega, \Phi)},$$  \hspace{1cm} (1)$$

where $\Phi$ is the angle of incidence (in our experiment $80^\circ$ with a beam divergence of $\pm 1.7^\circ$) and $\tilde{r}_p$ and $\tilde{r}_s$ are the complex Fresnel reflection coefficients for light which is polarized parallel ($p$) and perpendicular ($s$) to the plane of incidence, respectively. The dielectric function is extracted from $\tilde{\rho}(\omega, \Phi)$ by inverting the Fresnel equations:

$$\tilde{\varepsilon}(\omega) = \left[\frac{(1 - \tilde{\rho}(\omega, \Phi))}{(1 + \tilde{\rho}(\omega, \Phi))}\right]^2 \tan^2 \Phi \sin^2 \Phi + \sin^2 \Phi. \hspace{1cm} (2)$$

This inversion assumes an isotropic sample. For an anisotropic sample, in general, different elements of the dielectric tensor can contribute to $\tilde{\rho}(\omega, \Phi)$. The formal inversion according to Eq. (2) then yields only a so-called pseudodielectric function [25]. For the case of YBa$_2$Cu$_3$O$_{7-\delta}$, which is an almost uniaxial and strongly anisotropic material with metallic behavior of $\tilde{\varepsilon}_{a,b}(\omega)$ and insulating behavior of $\tilde{\varepsilon}_c(\omega)$, it was previously shown that the pseudodielectric function represents a very good approximation for $\tilde{\varepsilon}_c$ when the measurement is performed with the $c$-axis in the plane of incidence [26].

The technique of ellipsometry provides significant advantages over conventional reflection methods: i) it does not require the determination of the absolute intensity of the reflected light (no reference problem) and ii) the complex dielectric function $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ is obtained directly, no Kramers-Kronig transformation and thus no extrapolation of the reflectivity towards zero and infinite frequency is needed [27,28].

The ellipsometric measurements have been performed at the U4IR beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), using a home-built setup attached to a Nicolet Fast-Fourier Spectrometer [27,28]. The high brilliance of the synchrotron light source enables us to perform very accurate ellipsometric measurements in the far-infrared range even on samples with comparably small ac-faces of $0.5\times1$ mm$^2$. Since only relative intensities are required, the ellipsometric measurements are very reproducible and the data taken at a given temperature before and after thermal cycling or several days of measurement coincide to within the noise level.
III. RESULTS

1. Strongly underdoped YBa$_2$Cu$_3$O$_{6.5}$

Figure 2 shows the real part of the far-infrared (FIR) c-axis conductivity $\sigma_c(\omega,T)$ of the strongly underdoped YBa$_2$Cu$_3$O$_{6.5}$ crystal with $T_c=52$ K for (a) $T=300$, 200, and 150 K and (b) $T=150$, 110, 60, 45, 35 and 4 K. At room temperature the six infrared-active phonon modes at 155, 190, 280, 320, 560 and 630 cm$^{-1}$ are superimposed on a weak and almost featureless electronic background. As the temperature is lowered below room-temperature, the electronic background decreases continuously and develops the so-called normal-state gap (NS gap) or pseudogap which is a well known feature of the underdoped cuprate superconductors \cite{2,29-32}. Evidently, this NS-gap starts to develop at some rather high temperature, $T_{NG} \geq 300$ K. Its characteristic frequency scale $\omega_{NG}$ is fairly large and it even exceeds the measured spectral range, i.e., $\omega_{NG} > 700$ cm$^{-1}$ \cite{31,32}. Figure 2 shows that the gradual onset of the renormalization of the oxygen bond-bending mode at 320 cm$^{-1}$ and the additional broad peak at 410 cm$^{-1}$ occurs around $T^* \sim 150$ K, i.e., well below $T_{NG} \geq 300$ K but also well above $T_c=52$ K. However, the most important feature that is evident in Fig. 2b is that both, the anomaly of the 320 cm$^{-1}$ phonon mode and the formation of the additional absorption peak at 410 cm$^{-1}$, exhibit very pronounced and steep changes right at $T_c=52$ K. This finding implies that both effects are related to the superconducting transition rather than to the NS-gap or to the spin-gap phenomenon as has been previously suggested \cite{3,9}. The gradual onset of the anomalies at $T^* \gg T_c$ may be due to superconducting pairing fluctuations (especially within the bilayers) which become particularly pronounced for strongly underdoped and thus very anisotropic samples. We do not attempt here to comment on the rather controversial question of whether the NS-gap and/or the spin gap are also somehow related to the superconducting pairing fluctuations.

We have performed a more quantitative data analysis by fitting to the complex dielectric function in the spectral range 250$<\omega<700$ cm$^{-1}$ a sum of modified Lorentzian functions
\( \epsilon(\omega) = S \cdot (\omega_o^2 + i\Gamma \cdot Q)/(\omega_o^2 - \omega^2 - i\omega \cdot \Gamma) \) which represent the contributions of the phonon modes at 280, 320, 560 and 630 cm\(^{-1}\). This modified Lorentzian function which is obtained by mixing the real- and the imaginary parts of the usual Lorentzian function (it basically corresponds to a Fano-like function) allows one to perform Kramers-Kronig consistent fits of asymmetric phonon lineshapes \([2,3]\). In agreement with previous reports \([2,3]\), we find that only the phonon modes at 560 and 630 cm\(^{-1}\) are very asymmetric and that the asymmetry \(Q\) of these modes increases with decreasing temperature. In order to describe the flat electronic background and the additional broad absorption peak in a Kramers-Kronig consistent way we have also included a sum of seven broad Lorentzian oscillators which have been located between 250 and 700 cm\(^{-1}\) and whose half-widths have been limited to values between 150 and 500 cm\(^{-1}\).

In our opinion this fitting procedure does not allow one to obtain an appropriate description of the phonon contribution since it assumes that all the ions participating in the phonon modes experience the same (average) electric field. Instead, as motivated in Ref. \([12]\), we suggested that the local electric fields acting on the ions exhibit significant deviations from the average field as a result of the extremely weak electronic coupling between the individual CuO\(_2\) planes of underdoped cuprates. We have shown that the spectacular anomaly of the 320 cm\(^{-1}\) phonon mode, and also the asymmetry and the SW changes of the phonon modes at 560 and 630 cm\(^{-1}\), can be explained by such local field effects, in particular, by the changes of the local electrical fields caused by the onset of Josephson-effects within the intra- and inter-bilayer junctions \([12]\). In the present paper we nevertheless apply the simpler fitting procedure using modified Lorentzian functions in order to obtain the temperature dependence of the parameters of the phonon modes which can be readily compared with previous results.

Figure 3 shows the temperature dependence of (a) the oscillator strength \(S\), (b) the eigenfrequency \(\omega_o\), and (c) the half-width \(\Gamma\) of the oxygen bond-bending mode at 320 cm\(^{-1}\). It is evident from Fig. 3a and 3b that the changes of \(S\) and \(\omega_o\) set in rather gradually around \(T^* \sim 150\) K. The temperature dependences of both quantities, however, exhibit a sudden
and steep change around $T_c=52$ K. This finding contrasts with the previous reports that the renormalization of the 320 cm$^{-1}$ phonon mode does not exhibit any noticeable change around $T_c$ [3,9]. In agreement with the previous reports we find that the half-width $\Gamma$ of the 320 cm$^{-1}$ mode starts to decrease only below $T_c=52$ K [1–3,33]. For $T^* > T > T_c$ it even tends to increase, but this small increase may be an artifact of our fitting procedure. Figure 4 displays the electronic background including the additional peak around 400 cm$^{-1}$ which has been obtained by subtracting the contributions of the phonon modes at 280, 320, 560 cm$^{-1}$ and 630 cm$^{-1}$. The formation of the additional peak show in Fig. 4 follows a similar temperature dependence like the anomaly of the 320 cm$^{-1}$ phonon mode. The broad peak gradually develops below $T^* \sim 150$ K and suddenly increases in magnitude below $T_c=52$ K. Evidently, the peak position does not change much as a function of temperature. Below $T_c$ the peak is very pronounced and therefore hardly affected by the subtraction of the phononic contribution. The frequency of the maximum decreases slightly from 410 cm$^{-1}$ at 5 K to 395 cm$^{-1}$ at 45 K. Above $T_c$ the peak becomes rather weak as compared to the phonon mode at 320 cm$^{-1}$. We therefore cannot reliably determine its position. Nevertheless it is evident that it remains close to 400 cm$^{-1}$. Note that within the Josephson-superlattice-model the peak position is expected to decrease only by about 30 cm$^{-1}$ as the temperature is increased above $T_c$. The position of the transverse plasmon is determined mainly by the intra-bilayer Josephson-frequency which for strongly underdoped samples has been suggested not to exhibit any pronounced changes at $T_c$ since the pairing fluctuations within the individual bilayers persist far above the macroscopic critical temperature $T_c$.

Figure 5 shows a comparison of the temperature dependence of the spectral weight of the additional 410 cm$^{-1}$ peak, $SW^{410}$, (solid squares) with the spectral weight loss of the 320 cm$^{-1}$ phonon mode, $\Delta SW^{320}$, (open circles). The value of $\Delta SW^{320}$ has been calculated according to the formula $\Delta SW = \pi^2 c \cdot \epsilon_o \cdot [S(175K) - S(T)] \cdot \nu_o^2$ using the oscillator strenghts $S(T)$ and the eigenfrequencies $\nu_o$ given in Fig. 3a and 3b. The error bar indicates the upper limit for the spectral weight loss of the apical oxygen mode at 560 cm$^{-1}$. The inset of Fig. 5 illustrates how we have estimated the spectral weight of the additional peak $SW^{410}$ (shaded
area) by integrating the conductivity between 220 and 680 cm\(^{-1}\) (open circles) and subtracting the contribution of a linear electronic background (solid line). Note that our assumption of a linear electronic background conductivity is supported by the high temperature data for \(T>T^*\) =150 K (see Fig. 4a) and by the data for less strongly underdoped samples where the additional peak is comparably weak and appears only below \(T_c\) (see Ref. [31,32] and discussion below). It is evident from Fig. 5 that the spectral weight losses of the phonon modes at 320 and 560 cm\(^{-1}\) account only for some fraction of the spectral weight of the additional absorption peak at 410 cm\(^{-1}\). We estimate that at least 40-50\% of the spectral weight of the additional absorption peak does not arise from the phonon subsystem but instead seems to arise from the electronic continuum. Such a redistribution of the electronic spectral weight towards the additional absorption peak is predicted by the Josephson-superlattice-model where the transverse Josephson plasmon acquires a sizeable fraction of the spectral weight of the SC condensate [11,12]. This means that some fraction of the spectral weight removed in the FIR-regime does not appear in the delta-function at zero frequency which describes the inductive response of the superfluid condensate but is instead shifted to the additional absorption peak representing the transversal Josephson plasmon. In fact, our choice of the linear electronic background (solid line) is rather conservative. Also shown in the inset is a fit with a Lorentzian plus a linear electronic background conductivity (dashed lines) which gives a somewhat larger value of \(\text{SW}^{410} \approx 16.000 \, \Omega^{-1}\text{cm}^{-2}\) at \(T=5\) K. The result of this fit agrees surprisingly well with the prediction of the Josephson-superlattice model that the SW of the bare transverse Josephson-plasmon (neglecting the interaction with the phonons and the consequent redistribution of the spectral weight of the 320 cm\(^{-1}\) phonon mode, \(\Delta\text{SW}^{320}(5K) \approx 5000 \, \Omega^{-1}\text{cm}^{-2}\)) should be around 10.000 \(\Omega^{-1}\text{cm}^{-2}\) [12].

It has been reported previously that the spectral weight of the additional absorption peak can be fully accounted for by the spectral weight loss of the phonon modes at 320 and 560 cm\(^{-1}\) [2]. We note that this discrepancy between the conclusions of [2] and ours does not arise from any significant differences in the experimental data but rather originates from the difference in the estimate of the electronic background. It seems that Homes et
al. obtained a lower spectral weight of the additional absorption peak by introducing an
electronic background which develops a gap-like feature around 280 cm$^{-1}$ (see for example
Fig. 10 of Ref. [2]). They argued that this gap feature is related to the NS gap. Our recent
ellipsometric data, however, do not support such an interpretation because they show that
the onset frequency of the NS gap, $\omega_{NG}$, is significantly larger: it increases from $\omega_{NG} \approx 650$
cm$^{-1}$ for slightly underdoped samples to $\omega_{NG} > 700$ cm$^{-1}$ for strongly underdoped samples.
We have also shown that the temperature at which the signatures of the normal state NS-gap
start to appear increases rather rapidly on the underdoped side and even exceeds room
temperature for strongly underdoped samples [31,32] (see also Fig.2). Note that recent
ARPES- and tunneling experiments yield a similar temperature- and doping dependence
of the NS-gap (even the absolute values of the gap size agree reasonably well) [34–37]. This fact
allows us to conclude that the characteristic energy- and temperature scales of the additional
absorption peak and the NS-gap (and also their doping dependence) are very different which
makes it rather unlikely that both have a common origin.

2. Moderately underdoped YBa$_2$Cu$_3$O$_{6.75}$

We have also performed FIR ellipsometric measurements on a less strongly underdoped
YBa$_2$Cu$_3$O$_{6.75}$ sample with $T_c=80$ K. Figure 6 shows its c-axis conductivity $\sigma_c(\omega,T)$ at
different temperatures between 300 and 10 K. The anomaly of the oxygen bond-bending
mode at 320 cm$^{-1}$ is significantly weaker than that of the strongly underdoped sample. The
additional absorption peak is located at higher frequencies (around 480 cm$^{-1}$) and it is less
pronounced. Figure 7 shows the temperature dependence of (a) the oscillator strength S,
(b) the eigenfrequency $\omega_o$ and (c) the half-width $\Gamma$ of the 320 cm$^{-1}$ phonon mode which have
been obtained using the fitting procedure outlined above. It can be seen that the onset of
the anomaly of the 320 cm$^{-1}$ mode occurs now close to the superconducting transition (i.e.,
$T^* \lesssim 100$ K). A similar result has been previously obtained from conventional reflection
measurements on weakly underdoped Y-123 crystals [3]. The formation of the NS-gap, as
evidenced from the gradual suppression of the electronic background conductivity, can be seen to set in at a significantly higher temperature $T_{NG} \gtrsim 200$ K and the characteristic frequency scale of the NS-gap still exceeds the measured spectral range, $\omega_{NG} > 700$ cm$^{-1}$. These findings support our point of view that the anomaly of the 320 cm$^{-1}$ mode and the formation of the additional absorption peak are not directly related to the mechanism that is responsible for the NS-gap [31,32]. Figure 8 shows the electronic background including the additional absorption peak which has been obtained by subtracting the contributions of the phonon modes at 280, 320, 570 cm$^{-1}$ and 620 cm$^{-1}$ (as described above). Figure 9 shows the estimated T-dependences of the spectral weight of the additional peak at 480 cm$^{-1}$ (once more assuming a linear electronic background) and of the spectral weight loss ($\Delta SW$) of the phonon mode at 320 as estimated from the change in its oscillator strength according to: $\Delta SW = \pi^2 c \cdot \epsilon_o \cdot [S (120K) − S (T)] \cdot \nu_o^2$. In analogy to the strongly underdoped sample, a sizeable fraction of the spectral weight of the absorption peak does not seem to arise from the phonon subsystem.

A. Summary

In summary, we have performed ellipsometric measurements of the FIR $c$-axis conductivity of underdoped YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals. In particular, we have studied the temperature dependence of the spectacular anomaly of the oxygen bond-bending mode at 320 cm$^{-1}$ and of the additional absorption peak. For the strongly underdoped YBa$_2$Cu$_3$O$_{6.5}$ crystal with $T_c=52$ K the gradual onset of the anomaly of the 320 cm$^{-1}$ phonon mode and the growth of the additional absorption peak around 400 cm$^{-1}$ occur around $T^* \sim 150$ K, i.e., well below the onset temperature of the NS-gap, $T_{NG} \gtrsim 300$ K, but also well above $T_c=52$ K. Most remarkably, however, we find that both anomalies exhibit a very pronounced and marked change right at $T_c=52$ K. For a less strongly underdoped YBa$_2$Cu$_4$O$_{6.75}$ crystal with $T_c=80$ K both anomalies start to appear in the vicinity of the superconducting transition, $T^* \sim T_c=80$ K while the signatures of the NS-gap appear already below $T_{NG} \gtrsim 200$ K. Our
measurements thus establish that both anomalies are related to the superconducting transition. For strongly underdoped and thus very anisotropic samples, the gradual onset of the anomalies may occur well above $T_c$ due to superconducting pairing fluctuations within the individual bilayers, but there is always a steep and sudden increase of both anomalies when the macroscopically coherent superconducting state forms at $T_c$. This implies that the anomalies are not related to the NS-gap in the c-axis conductivity nor to the spin-gap phenomenon as observed in NMR- and NQR-measurements both of which exhibit no noticeable changes at $T_c$. For both underdoped crystals a sum-rule analysis of the changes of the spectral weights indicates that the spectral weight of the additional absorption peak is not fully accounted for by the spectral weight loss of the phonon modes at 320 and 560 cm$^{-1}$. At least 40-50 % of the spectral weight of the additional absorption peak seems to arise from the electronic background, namely from the superconducting condensate. We have outlined that all the reported features are compatible with a recently proposed model where the bilayer cuprate compounds such as Y-123 are treated as a superlattice of inter- and intra-bilayer Josephson-junctions. The additional absorption peak can be related to the transverse optical plasmon, while the spectacular phonon anomaly can be explained as due to the drastic changes of the local electrical fields acting on the in-plane oxygen ions as the Josephson current sets in below $T_c$ for the inter-bilayer junctions while below $T^* \geq T_c$ for the intra-bilayer junctions.

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V. FIGURE CAPTIONS

Figure 1: Temperature dependence of the zero-field-cooled (zfc) and field-cooled (fc) volume DC-magnetization, $\chi_V$, of the YBa$_2$Cu$_3$O$_{6.5}$ crystal (open circles) and the YBa$_2$Cu$_3$O$_{6.75}$ crystal (solid squares). The external field $H_{\text{ext}} = 5$ Oe was applied along the c-axis of the platelet shaped crystals. Corrections for demagnetization factors have not been taken into account. The critical temperatures and the transition width (between 10 and 90% of the diamagnetic shielding) are $T_c = 52$ K, $\Delta T_c = 3$ K and $T_c = 80$ K, $\Delta T_c = 4$ K.

Figure 2: Temperature dependence of the real part of the FIR c-axis conductivity of the strongly underdoped YBa$_2$Cu$_3$O$_{6.5}$ crystal with $T_c = 52$ K. Spectra are shown for (a) $T = 300$, 200 and 150 K and (b) $T = 150$, 60, 45, 35 and 5 K.

Figure 3: Temperature dependence of (a) the oscillator strength $S$, (b) the eigenfrequency $\omega_o$ and (c) the half width $\Gamma$ of the oxygen bond-bending mode of the strongly underdoped YBa$_2$Cu$_3$O$_{6.5}$ crystal ($T_c = 52$ K). The phonon parameters have been obtained by fitting modified Lorentzian functions to the complex dielectric function (as outlined in the text). The dashed line marks the superconducting transition temperature $T_c = 52$ K, the dotted line indicates the gradual onset of the renormalization of the phonon mode around $T^* \sim 150K$.

Figure 4: Temperature dependence of the electronic conductivity including the additional absorption peak at 410 cm$^{-1}$ (presumed to be also of electronic origin) of the strongly underdoped YBa$_2$Cu$_3$O$_{6.5}$ crystal with $T_c = 52$ K which has been obtained by subtracting the contributions of the phonon modes at 280, 320, 560 and 630 cm$^{-1}$.

Figure 5: Temperature dependence of the spectral weight of the additional absorption peak at 410 cm$^{-1}$ (SW$^{410}$, solid squares) and the spectral weight loss of the oxygen bond-
bending mode at 320 cm\(^{-1}\) \((\Delta SW_{320}, \text{open circles})\). The inset illustrates how the SW of the additional absorption peak has been obtained. The open circles represent the spectrum at T=5 K obtained after the phonons have been subtracted, the solid line represent the linear background which has been further subtracted in order to obtain SW\(^{410}\) as indicated by the shaded area. Also shown is a fit with a Lorentzian plus a linear background (dashed lines) which gives a somewhat larger value of SW\(^{410}\) \(\approx 16.000 \, \Omega^{-1} cm^{-2}\) at 5 K. The spectral weight loss of the 320 cm\(^{-1}\) phonon mode has been calculated according to the formula $\Delta SW_{320} = \pi^2 c \cdot \epsilon_o \cdot [S(175K) - S(T)] \cdot \nu_o^2$ using the oscillator strenght S(T) and the eigenfrequencies $\nu_o$ given in Fig. 3a and 3b. The error bar indicates the maximum spectral weight loss at T= 5K of the phonon mode at 560 cm\(^{-1}\).

Figure 6: Temperature dependence of the real part of the FIR c-axis conductivity of the weakly underdoped YBa\(_2\)Cu\(_3\)O\(_{6.75}\) crystal with $T_c=80$ K.

Figure 7: Temperature dependence of (a) the oscillator strength S, (b) the eigenfrequency $\omega_o$ and (c) the half width $\Gamma$ of the oxygen bond-bending mode of the moderately underdoped YBa\(_2\)Cu\(_3\)O\(_{6.75}\) crystal ($T_c=80$ K). The phonon parameters have been obtained by fitting modified Lorentzian functions to the complex dielectric function (as outlined in the text). The dashed line marks the superconducting transition temperature $T_c=80$ K.

Figure 8: Temperature dependence of the electronic conductivity, including the additional absorption peak around 480 cm\(^{-1}\), of the moderately underdoped YBa\(_2\)Cu\(_3\)O\(_{6.75}\) crystal with $T_c=80$ K which has been obtained by subtracting the contributions of the phonon modes at 280, 320, 570 and 620 cm\(^{-1}\).

Figure 9: Temperature dependence of the spectral weight of the additional absorption peak at 480 cm\(^{-1}\) (SW\(^{480}\), solid squares) and the spectral weight loss of the oxygen bond-bending mode at 320 cm\(^{-1}\) \((\Delta SW_{320}, \text{open circles})\). The spectral weight loss of the 320 cm\(^{-1}\) phonon mode has been calculated according to the formula $\Delta SW= \pi^2 c \cdot \epsilon_o \cdot [S(175K) - S(T)] \cdot \nu_o^2$, using the oscillator strenghts S(T) and the eigenfrequencies...
\( \nu_0 \) given in Fig. 7a and 7b. The error bar indicates the maximum spectral weight loss at \( T = 5\text{K} \) of the phonon mode at 570 cm\(^{-1} \).
$S$

$T_c$  $T^*$

$\omega_0 [\text{cm}^{-1}]$

$\Gamma [\text{cm}^{-1}]$

$T [\text{K}]$
The figure illustrates the temperature dependence of the electrical conductivity, \( \sigma_{1c} \), as a function of frequency, \( \nu \), for different temperatures. The upper graph shows \( \sigma_{1c} \) in units of [\( \Omega^{-1} \cdot \text{cm}^{-1} \)] for temperatures of 300 K (solid line), 175 K (dashed line), and 150 K (dotted line). The lower graph presents \( \sigma_{1c} \) for temperatures ranging from 4 K to 175 K, with each temperature represented by a different line style.
$SW^{410}, \Delta SW^{320} \left[ 10^3 \Omega^{-1} \text{cm}^{-2} \right]$
