Direct evidence of a bulk nodal gap in the overdoped regime of Y\textsubscript{0.9}Ca\textsubscript{0.1}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} thin films from THz spectroscopy

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Abstract - We measured the terahertz (THz) complex conductivity of Ca-doped YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} thin films in the frequency range of 0.1 to 3THz (3 to 100cm\textsuperscript{-1}) and in the temperature range of 20 to 300K. The films were measured using time domain and frequency domain THz spectroscopy methods. We show evidences for the existence of an additional energy sub-gap in overdoped Y\textsubscript{0.9}Ca\textsubscript{0.1}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} samples. The evidences for this gap appear as a sharp decrease in the real part of the optical conductivity, \(\sigma_1(\omega,T)\), and as a dip in the imaginary part of the optical conductivity multiplied by frequency, \(\omega\sigma_2(\omega,T)\). These features are observed at a frequency equivalent to an energy of 1.2meV. Our complex conductivity spectra are in agreement with the theoretical prediction assuming a mixed symmetry order parameter (SCHÜRRER I. et al., Physica C, 303 (1998) 287). We suggest that these observations are direct evidence of a nodal gap obtained in a \(d_{x^2-y^2}\)-wave superconductor when adding an imaginary \(s\) or \(d_{xy}\) bulk component in the overdoped regime.

Symmetry of the order parameter (OP) in high-\(T_c\) cuprate superconductors is an important question, yet unresolved [1]. Unlike in conventional superconductors, in high-\(T_c\) cuprates there are many indications supporting an anisotropic symmetry exhibiting nodes in the OP, i.e. \(d_{x^2-y^2}\)-wave symmetry [2,3]. However, there is some degree of consensus that the \(d_{x^2-y^2}\)-wave pairing symmetry also includes an extra imaginary component.

This extra component is still puzzling and leads us to important questions that remain unresolved. Tunneling [4–6] measurements of optimally doped YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} films in magnetic fields and penetration depth [7] measurements of overdoped Y\textsubscript{1-x}Ca\textsubscript{x}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} films show an additional imaginary component estimated to be of the order of \(\delta \approx 2\)meV. It has recently been shown that an extra imaginary component also exists in YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} nano islands on a single electron transistor [8] and in underdoped cuprates thin films measured by ARPES technique [9,10]. Other ARPES [11] and Tricrystal geometry [12] measurements on overdoped and optimally doped YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} crystals show a robust \(d_{x^2-y^2}\)-wave pairing symmetry.

One of the key questions in the current research is whether this imaginary component is a surface effect [13] or whether it is in fact a bulk property [14]. Some of the proposed models require pure bulk \(d_{x^2-y^2}\)-wave symmetry [15–18], while others do not [19–21]. Others suggest an anisotropy of the symmetry with a subdominant real s-wave part in the \(a-b\) planes and a pure s-wave in the \(c\)-axis [22]. Nevertheless, bulk mixed states such as \(d_{x^2-y^2} + is\) or \(d_{x^2-y^2} + id_{xy}\) are allowed within the symmetries of YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} [23]. This distinction bare important implications for our understanding of the high-\(T_c\) superconductivity mechanism.

The progress made in THz spectroscopy in the last few years made it possible to probe bulk material properties...
at low energies in a reproducible and accurate manner. Our work is focused on probing the complex conductivity of overdoped $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7−\delta}$ thin films, where the energy scale of the THz radiation is equivalent to the energy scale of an additional imaginary component, $2\delta \approx 4\text{meV} \approx 32\text{cm}^{-1}$. As will be further elaborated, we tried to identify the frequency and temperature dependence of the complex conductivity in order to obtain the order parameter symmetry in our samples. We show direct evidence for this additional imaginary component in our complex conductivity spectra which is consistent with the theoretical prediction of Schürer et al. [24] and results from direct measurement of the bulk material properties.

**Experimental.** — In this paper we investigate two batches of $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7−\delta}$ thin films. The films were deposited by a DC sputtering method at a growth temperature of 820°C, using a pressure template procedure [25] including additional water vapor partial pressure of 2–3 mTorr. The typical film thickness is 50–60 nm on 1 mm thick LaAlO$_3$ substrates. XRD measurements show well oriented c-axis films. The samples’ transition temperature was measured using resistance and induction methods. The films showed typical $T_c$ of 78 K ± 1 K. From the curvature of resistivity as a function of temperature, we have deduced that the samples are in the overdoped regime. This is done by taking the second derivative of the resistivity curve as a function of temperature.

The first batch of films was measured using a Time Domain THz Spectroscopy method applying a TeraView TPS Spectra 1000™ system. The time Domain THz spectroscopy method has been reviewed in several papers (see for instance [26,27]). The complex transmission spectra of the films, substrate and reference (clear aperture) were recorded at room temperature down to 20 K with steps of about 1 K and in the frequency range of 0.1–3 THz (3–100 cm$^{-1}$). As will be elaborated further, a unique low frequency behavior was obtained in the complex conductivity data.

In order to explore the low frequency regime, a second batch of films was measured using a different THz spectroscopy method, i.e. quasi-optical Mach-Zehnder interferometer setup. This is a well-known method, which has been reviewed and used by several groups (see for instance [28,29]). The absolute transmission coefficient and the transmission phase shift of the films, substrate and reference were recorded from room temperature down to 20 K, in steps of 50 K above 100 K and steps of 10 K below 100 K. The data was measured using Backward Wave Oscillator THz sources in frequency range of 2–4 cm$^{-1}$, 8–23 cm$^{-1}$ and 28–41 cm$^{-1}$.

The complex transmission in both methods was first analyzed for the bare substrate. The data for the LaAlO$_3$ substrate was fitted using a Lorentz oscillator for the phonon absorption at a resonance frequency of 190 cm$^{-1}$ [30] and resulted in an almost frequency and temperature-independent dielectric function with $\varepsilon_1 \approx 24$.

We used the two-fluid model to analyze the data of our superconducting films. The scattering rate, $\Gamma$, and plasma frequency of the quasi-particles, $\omega_{p_n}$, and plasma frequency of the superconducting carriers, $\omega_{p_s}$, were determined by a least-square fitting of the transmission and phase shift spectrum from which the complex conductivity was deduced [31]. In order to achieve the best fit, we have minimized the goodness of fit parameter, $\chi^2$, by additionally tuning our fit parameters as a function of frequency using the Variable Dielectric Function [32] for the THz-TDS data and Fresnel equations [33] for the Quasi-Optical system data.

**Results and discussion.** — THz transmission of $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{7−\delta}$ films is shown in fig. 1 and in fig. 2(a) for the time domain and frequency domain measurements, respectively. Above $T_c$ the temperature dependence of a complex transmission function is defined mainly by a decrease in its absolute value. Below $T_c$, with the sharp decrease of transmission amplitude, there is also a change in transmission phase shift (fig. 1 and fig. 2(b)).

To extract the complex conductivity out of the transmission data, we have used the transmission function of four interfaces, i.e. a sample with two layers. The two-fluid model was used to describe the complex conductivity of the thin film:

$$\hat{\sigma}(\omega, T) = \hat{\sigma}_n(\omega, T) + \hat{\sigma}_s(\omega, T),$$  

(1)

where $\sigma_n$ is the complex conductivity of the normal carriers given by

$$\hat{\sigma}_n(\omega, T) = \omega p_n(T) \left[ \frac{\Gamma_n(T)}{\Gamma_n^2(T) + \omega^2} + i \frac{\omega}{\Gamma_n^2(T) + \omega^2} \right],$$  

(2)

and $\sigma_s$ is the complex conductivity of the superconducting carriers given by

$$\hat{\sigma}_s(\omega, T) = \omega p_s(T) \left[ \delta(\omega = 0) + i \frac{1}{\omega} \right].$$  

(3)
Direct evidence of a bulk nodal gap in the overdoped regime of Y\(_{0.9}\)Ca\(_{0.1}\)Ba\(_2\)Cu\(_3\)O\(_{7-\delta}\) etc.

The data analysis focused mainly on the change in the scattering rate and the change in the plasma frequencies for both types of carriers as a function of temperature. Our analysis of the complex transmission data results in the fitting parameters’ temperature dependence as shown in fig. 3. Above \(T_c\), \(\Gamma\) decrease as temperature decreases while \(\omega_{p_n}\) maintains a constant value [34] and \(\omega_{p_s} = 0\). This behavior is well understood in the normal state. Below \(T_c\), the sharp decrease in \(\Gamma\) is related to condensation of normal carriers into the superconducting state while an increase in \(\omega_{p_s}\) is consistent with the formation and increase of superconducting carriers. Our analysis shows that at low temperatures \(\Gamma\) maintains a somewhat fixed value, consistent with other reports [35]. However, \(\omega_{p_n}\) starts to decrease or at least saturates at the same temperatures.

After applying the frequency-independent parameters of the two-fluid model as a first approach, we can deploy other approaches to tune our fitting parameters for achieving the best fit. In the frequency domain we have used Fresnel’s equations [33] and in the time domain we have used the Variable Dielectric Function [32] for the film’s data. These approaches enable to obtain better agreement between our data points and a general two-fluid model allowing frequency dependence of \(\Gamma\), \(\omega_{p_n}\), and \(\omega_{p_s}\).

The general behavior of the complex conductivity in our films is shown in fig. 4 and fig. 5 for the two spectroscopy methods. Above \(T_c\), the real part of conductivity, \(\sigma_1(\omega, T)\), slightly increases as the temperature decreases and is almost frequency independent. This increase is not followed by any change in the imaginary part of conductivity, \(\sigma_2(\omega, T)\). This behavior is attributed to the change of \(\Gamma\) with temperature. Below \(T_c\), a drastic change in \(\Gamma\) at the transition is causing the spectral weight to be quenched down to lower frequencies. As a result, a sharp increase is obtained in \(\sigma_1(\omega, T)\). The additional change at lower temperatures is attributed to the removal of additional
The above behavior is followed by some unique and new features in the low frequency regime. In a d-wave superconductor, $\sigma_1(\omega, T)$ should increase or at least retain a maximum value at low frequencies well below the energy gap, $\Delta$ [34]. However, a sharp decrease of $\sigma_1(\omega, T)$ is observed at low frequencies, at about 100 cm$^{-1}$ as shown in figs. 4 and 5(a). The onset drop in $\sigma_1(\omega, T)$ is observed as a dip in $\omega \sigma_2(\omega, T)$, which is proportional to $\omega_p$ (eq. (3)) and shown in fig. 6 for these overdoped samples at about the same frequency. This behavior appears below 50 K and seems to be enhanced as temperature decreases to the lowest measured temperature while it is smeared out above 50 K.

This non-monotonic behavior of $\sigma_1(\omega, T)$ and $\omega \sigma_2(\omega, T)$ at low frequencies can be related to a frequency dependence of $\Gamma$ or $\omega_p$, which deviates from the values shown in fig. 3. A decrease in $\sigma_1(\omega, T)$ can be explained as an increase in $\Gamma$ or as a decrease in $\omega_p$, at about 10 cm$^{-1}$. However, the increase in the scattering rate can be ruled out given the well-known behavior of scattering which achieves a constant value once the impurity limit is reached at low temperatures. Instead, we suggest that this decrease in conductivity is related to a decrease in $\omega_p$.

The decrease in $\sigma_1(\omega, T)$ and the dip in $\omega \sigma_2(\omega, T)$ at about 10 cm$^{-1}$ are inconsistent with a pure $d_{x^2-y^2}$-wave superconductor analyzed by the generalized two-fluid model. This inconsistency was observed in another $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_7-\delta$ films in addition to the above results. It was also observed in a $Y_{0.95}Ca_{0.05}Ba_2Cu_3O_7-\delta$ thin film, however less pronounced as in the 10% Ca-doped samples. On the contrary, this non-monotonic behavior was not observed in optimally doped samples that were measured in the same frequency range [38,39]. We argue...
that this sub-gap is more pronounced once the sample reaches a deeper overdoped state. In addition, time domain methods are less sensitive at sub-THz frequencies compared to the frequency domain method using BWO sources, therefore previous spectroscopy reports could not show this behavior.

As noted earlier, we can relate the change in the complex conductivity to a change of $\omega_p$, as a function of frequency which is proportional to the QP density of states (QDOS). Therefore, a change in the DOS should affect the complex conductivity. For the cases of pure $d_{x^2-y^2}$-wave symmetry or admixture of small subdominant real $s$-wave part, there are states down to zero energy, therefore no drastic change should be observed in the conductivity spectrum. However, for the complex symmetries $d_{x^2-y^2} + is$ and $d_{x^2-y^2} + id_{xy}$, which exhibit a node removal, there are no states available below a cut-off energy. Therefore, the sharp decrease in the DOS should be observed as a decrease in the concentration of quasi-particles, or experimentally by a decrease in $\omega_p$. As the real part of conductivity is a direct probe of the QP plasma frequency, a decrease in its value is observed at this cut-off energy, and therefore also at the energy of the imaginary component mentioned above.

The idea of an additional imaginary component in a superconducting order parameter was examined theoretically in calculating the complex conductivity by Schirrer et al. [24]. Several QDOS spectra were calculated for various imaginary and real part ratios. In the case of $s + id$ symmetry (see fig. 7) and assuming that the QDOS yields the absolute value of the order parameter, the results of Schirrer et al. are consistent with our data and show no evidence for a $d + s$ symmetry in our films. $\sigma_1(\omega, T)$ shows non-monotonic behavior followed by a decrease at low frequencies equivalent to the secondary gap energy. The imaginary part product, $\omega \sigma_2(\omega, T)$, shows a dip developing at the same energy as the onset frequency in $\sigma_1(\omega, T)$.

As noted before, the complex conductivity data in our films, which deviates from the pure $d_{x^2-y^2}$-wave and the frequency-independent parameters of the two-fluid model analysis, exhibits the features described above. We believe that the only possible interpretation of these deviations can be achieved by an additional imaginary part of the order parameter, as suggested by Schirrer et al.

Finally, we would like to clarify at this point that the decrease in $\sigma_1(\omega, T)$ at about 10 cm$^{-1}$, which is assumed to be the nodal gap energy, is at a much lower energy than the imaginary component measured directly by tunneling or obtained indirectly by microwave London penetration depth to have a value of about $\delta \approx 2$ meV (or $\approx 16$ cm$^{-1}$) [7]. We cannot rule out a possible explanation of this discrepancy where this extra imaginary gap component is a surface effect which reduces once a bulk is examined. In addition, the energy of the mentioned features in the complex conductivity were observed at a temperature range having a larger equivalent thermal energy. As expected, in this temperature range, these features are smeared, i.e. much broader as a function of frequency.

**Conclusions.** – The complex conductivity of two typical Ca-overdoped YBa$_2$Cu$_3$O$_{7-\delta}$ thin films was measured by both frequency and time domain spectroscopy techniques in the THz frequency range. We have shown distinct evidence for a sub energy gap in the THz frequency range which develops below $T_c$ and exhibits itself as a significant decrease in the real part of conductivity with a typical onset frequency of 10 cm$^{-1}$. The sub-gap in the real part of the conductivity shows up as a dip in $\omega \sigma_2(\omega, T)$ at the same frequency, reflecting a decrease in the superconducting plasma frequency. These features in the measured complex conductivity spectrum match the spectrum calculated by Schirrer et al. using a complex order parameter with an imaginary part of $2\delta \approx 1.2$ meV. We suggest that this gap is related to node removal in the overdoped regime of Y$_{0.9}$Ca$_{0.1}$Ba$_2$Cu$_3$O$_{7-\delta}$. This idea has previously
been reported utilizing various surface-sensitive tunneling experiments and microwave indirect measurements. However, this gap appears at lower energies than the one reported previously. The mentioned behavior was observed at thermal energies larger than the typical energies of the mentioned sub-gap which caused smearing effects up to about 50 K where mentioned effects disappear. At the current stage we cannot rule out the effect of Ca atoms, which might act as impurity centers causing localization. This could be done by a future research in which the Ca-doped samples are annealed into the optimal doped regime.

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REFERENCES

[1] Deutscher G., Rev. Mod. Phys., 77 (2005) 100.
[2] Dagan Y., Krupke R. and Deutscher G., Phys. Rev. B, 62 (2000) 146.
[3] Tsuei C. and Kirtley J., Physica C, 341-348 (2000) 1625.
[4] Krupke R. and Deutscher G., Phys. Rev. Lett., 83 (1999) 4634.
[5] Sharoni A., Millo O., Kohan A., Dagan Y., Beck R., Deutscher G. and Koren G., Phys. Rev. B, 65 (2002) 134526.
[6] Dagan Y., Krupke R. and Deutscher G., Europhys. Lett., 51 (2000) 116.
[7] Farber E., Deutscher G., Gorshunov B. and Dressel M., Europhys. Lett., 67 (2004) 834.
[8] Gustafsson D., Golubev D., Fogelström M., Claeson T., Kubatkin S., Bauch T. and Lombardi F., Nat. Nanotechnol., 8 (2013) 25.
[9] Fournier D., Levy G., Penne C., Mcchesney J. L., Bostwick A., Rottenberg E., Liang R., Hardy W. N., Bonn D. A., Elfmov I. S. and Damascelli A., Nat. Phys., 6 (2010) 905.
[10] Razzoli E., Drachuck G., Keren A., Radovic M., Plumb N. C., Chang J., Huang Y.-B., Ding H., Mesot J. and Shi M., Phys. Rev. Lett., 110 (2013) 047004.
[11] Damascelli A. and Shen Z.-X., Rev. Mod. Phys., 75 (2003) 473.
[12] Tsuei C., Kirtley J., Hammerl G., Mannhart J., Raffy H. and Li Z., Phys. Rev. Lett., 93 (2004) 187004.
[13] Fogelström M., Rainer D. and Sauls J. A., Phys. Rev. Lett., 79 (1997) 281.
[14] Dagan Y. and Deutscher G., Europhys. Lett., 57 (2002) 444.
[15] Pines D., Physica C, 235-240 (1994) 113.
[16] Pines D. and Monthoux P., J. Phys. Chem. Solids, 56 (1995) 1651.
[17] Anderson P. W., Science, 235 (1987) 1196.
[18] Anderson P. W., Baskaran G., Zou Z., Wheatley J., Hsu T., Shastry B. S., Doucot B. and Liang S., Physica C, 153-155 (1988) 527.
[19] Sachdev S., Physica A, 313 (2002) 252.
[20] Friedel J. and Kohmoto M., Int. J. Mod. Phys. B, 15 (2001) 511.
[21] Sangiovanni G., Capone M., Caprara S., Castellani C., Di Castro C. and Grilli M., Phys. Rev. B, 67 (2003) 174507.
[22] Müller K. A., Nature, 377 (1995) 133.
[23] Wenger F. and Östlund S., Phys. Rev. B, 47 (1993) 5977.
[24] Schürer I., Schachinger E. and Carbotte J., Physica C, 303 (1998) 287.
[25] Krupke R., Azoulay M. and Deutscher G., Sputtering of Y1Ba2Cu3O7−δ in Second-Generation HTS Conductors, edited by Goyal A. (Springer, US) 2005, pp. 97–108.
[26] Schmuttenmaer C. A., Chem. Rev., 104 (2004) 1759.
[27] Grischikowsky D., Keiding S., van Exter M. and Fattinger C., J. Opt. Soc. Am. B, 7 (1990) 2006.
[28] Gorshunov B., Volkov A., Spektor I., Prokhorov A., Mukhin A., Dressel M., Uchida S. and Loidl A., Int. J. Infrared Millim. Waves, 26 (2005) 1217.
[29] Pronin A. V., Dressel M., Pimenov A., Loidl A., Roshchin I. V. and Greene L. H., Phys. Rev. B, 57 (1998) 14416.
[30] Abrashev M. V., Litvinchuk A. P., Iliiev M. N., Meng R. L., Popov V. N., Ivanov V. G., Chakalov R. A. and Thomsen C., Phys. Rev. B, 59 (1999) 4146.
[31] Berlinsky A. J., Kallin C., Rose G. and Shi A.-C., Phys. Rev. B, 48 (1993) 4074.
[32] Kuzmenko A. B., Rev. Sci. Instrum., 76 (2005) 083108.
[33] Dressel M. and Grüner G., Electrodyamics of Solids, 1st edition (Cambridge University Press) 2002.
[34] Basov D. N. and Timusk T., Rev. Mod. Phys., 77 (2005) 721.
[35] Djordjevic S., Farber E., Deutscher G., Bontemps N., Durand O. and Contour J., Eur. Phys. J. B, 25 (2002) 407.
[36] Frenkel A., Gao F., Liu Y., Whitaker J. F., Uher C., Hou S. Y. and Phillips J. M., Phys. Rev. B, 54 (1996) 1355.
[37] Bachar N., THz properties of overdoped YBCO thin films, MSc. Thesis, Hebrew University of Jerusalem (2009).
[38] Wilke I., Khazan M., Rieck C., Kuzel P., Jaekel C. and Kurz H., Physica C, 341-348 (2000) 2271.
[39] Khazan M., A. Conference proceedings of Terahertz Spectroscopy and its Application to the Study of High-Tc Superconductor Thin Films, PhD Thesis, University of Hamburg (2002).