The c-axis optical sum rule and possible new collective mode in La$_{2-x}$Sr$_x$CuO$_4$

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We present the c-axis optical conductivity $\sigma_{1c}(\omega, T)$ of underdoped ($x=0.12$) and optimally doped ($x=0.15$) La$_{2-x}$Sr$_x$CuO$_4$ from 4 meV to 1.8 eV obtained by a combination of reflectivity and transmission spectra. In addition to the opening of the superconducting gap, we observe an increase of conductivity above the gap up to 270 meV with a maximal effect at about 120 meV. This may indicate a new collective mode at a surprisingly large energy scale. The Ferrell-Glover-Tinkham sum rule is violated for both doping levels. Although the relative value of the violation is much larger for the underdoped sample, the absolute increase of the low-frequency spectral weight, including that of the condensate, is higher in the optimally doped regime. Our results resemble in many respects the observations in YBa$_2$Cu$_3$O$_{7-\delta}$.

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The charge transport between the CuO$_2$ planes in the high-$T_c$ cuprates forms one of the most intriguing puzzles of these materials. On the one hand the essential common physics seems to lie in the collective behavior of holes doped into a 2D Mott insulator, while the interplane conductivity strongly depends on the interlayer chemistry, which varies dramatically among different members of the high-$T_c$ family. On the other hand, it is the in-plane 'confinement' that preserves a possibility of significant lowering of the c-axis kinetic energy (KE) as the 3D coherent movement of the Cooper pairs is restored below $T_c$ [1,2], which, however, was shown to be a small effect in some single-layer compounds [3,4]. The models based on the KE lowering in the superconducting (SC) state predict the violation of the Ferrell-Glover-Tinkham (FGT) optical sum rule [5], which means that the spectral weight (SW) of the SC condensate is collected not only from energies of the order of 2$\Delta$ but also from higher frequencies. For the c-axis the violation has been experimentally tested in YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) over a broad doping range and a significant increase of the relative violation value was found in the underdoped regime [6]. In the case of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) a value of 50% has been reported for a slightly underdoped sample [7], although the doping dependence is still not known. Thus, the c-axis KE lowers in the SC state, which, however, leaves room for debate whether this is a by-product or the very reason for superconductivity [1,2,8,9].

The conclusiveness of the sum rule analysis greatly depends on a reliable value of $\sigma_1(\omega, T)$. However, the usually employed Kramers-Kronig (KK) analysis of reflectivity seriously lacks accuracy due to the insensitivity of reflection to small absorption details and an ambiguity of the data extrapolation. This is a major problem for LSCO with a relatively small c-axis electronic conductivity [10]. In this Letter we report on our optical study of underdoped (UD) and optimally doped (OpD) LSCO by a combination of reflection and transmission spectroscopy which overcomes many limitations of the KK analysis. We measured the transmission (E $||$ c) through free-standing thin crystals to avoid complications due to a substrate. Here we focus on the low-temperature data well below the HTT-LTO phase transition.

The La$_{2-x}$Sr$_x$CuO$_4$ single crystals ($x=0.12$, $T_c=29$ K and $x=0.15$, $T_c=37$ K) were grown by the same method as described in Ref. [11]. The c-axis was within 1$\degree$ in the ac sample surface, as determined by Laue diffraction. Initially the reflectivity (R) spectra (15 - 6000 cm$^{-1}$) have been obtained using an FT-IR spectrometer on thick samples with the surface area of 20-25 mm$^2$ mounted on a copper cone (see Fig.1(a)). The in-situ gold evaporation was used as a reference. The spectra match very well with the previous data [10], which were used to continue curves to higher frequencies. Then each sample was attached to a supporting plane and reduced to a thin platelet by polishing with diamond paper with a roughness down to 0.1 $\mu$m. The platelets were made 23 $\mu$m and 14 $\mu$m thick with areas of 1.3 and 1.0 mm$^2$ for $x=0.12$ and 0.15 correspondingly. The thickness was chosen in order to optimize the transmission sensitivity on the base of an anticipated value of $\sigma_1$. Finally the samples were unglued from the support and mounted on a copper mask. The c-axis transmission (T) spectra (see Fig.1(b)) have been measured using an FT-IR spectrometer (20 - 6000 cm$^{-1}$) and a grating-type spectrometer (6000 - 15000 cm$^{-1}$). At higher frequencies the samples are not transparent presumably due to the charge-transfer absorption, at lower energies the diffraction effects mask the data. The transmission for E $||$ a was unmeasurably small, indicating the absence of any 'pinhole' leakage. All the measurements were done in a home-made optical cryostat with a temperature-stable sample position. The absolute systematic error bars of R and T are about 0.01 and 0.03 respectively. The accuracy of their relative temperature difference, is at least one order of magnitude better. The temperature precision is about 1 K [12].
The measured $R(\omega)$ and $T(\omega)$ are functions of $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$:

$$R = |r|^2, T = \left| \frac{(1 - r^2)t}{1 + r^2t^2} \right|^2, r = \frac{1 - \sqrt{c}}{1 + \sqrt{c}}, t = e^{\frac{i\pi}{2}\sigma d},$$

where $d$ is the sample thickness. These relations can be applied to derive $\epsilon_1$ and $\epsilon_2$ from $R$ and $T$ for frequencies above 650 cm$^{-1}$ and below 200 cm$^{-1}$ without the use of the KK transformation. In the phonon range, where $T$ is vanishingly small, the KK method still should be exploited. Here we use a more accurate analysis (which we call 'RT+KK'), which is to find an $\epsilon(\omega)$ which satisfies the KK relations and delivers the best fit to the experimental $R(\omega)$ and $T(\omega)$ simultaneously in the whole spectral range. It is done by modelling $\epsilon(\omega)$ with a very large number of oscillators (approaching the number of experimental points), including the zero-frequency lossless mode of the SC condensate. The sample thickness is one of the variable parameters which is determined by fitting of the Fabry-Perot fringes [15]. The two methods give close results. The optical conductivity $\sigma_1(\omega) = \omega\epsilon_2(\omega)/4\pi$ is shown in Fig.1(c). Notably, above 1000 cm$^{-1}$ it is significantly smaller than the previously published values based solely on the KK analysis [13,14] (see inset in Fig.1(c)).

![Graphs showing energy and optical properties](image)

**Fig. 1.** The c-axis reflectivity (a), transmission (b) and optical conductivity (c) of the UD ($x=0.12$) and the OpD ($x=0.15$) LSCO samples. The same colors at the same doping correspond to the same temperature. The inset compares $\sigma_1(\omega, 300K)$ (red) with the previous results based on the KK analysis (Ref. [13] - blue, Ref. [14] - green).

The conductivity for selected frequencies is shown in Fig.2(a). It is temperature-dependent both in the normal and the SC state and shows a distinct kink right at $T_c$. Because $\sigma_1(\omega, T)$ has a strong temperature dependence above $T_c$, the difference $\Delta \sigma_1 = \sigma_1(T = T_c) - \sigma_1(T \ll T_c)$ does not represent purely a superconductivity induced change of $\sigma_1(\omega)$. Instead, we use the *slope jump* at $T_c$

$$\Delta_\sigma \sigma_1 \equiv \left. \frac{\partial \sigma_1}{\partial T} \right|_{T_c+} - \left. \frac{\partial \sigma_1}{\partial T} \right|_{T_c-}$$

(2)

to characterize the effect of the SC transition. One can see that the kink is negative at low frequencies, indicating the opening of the SC gap. However, it becomes positive at somewhat higher energies ($\sim 1000$ cm$^{-1}$, or $\approx 120$ meV) and disappears within the noise level above $\Omega_c \approx 2200$ cm$^{-1}$ ($\approx 270$ meV). The ‘anomalous’ kink at
intermediate energies is nicely seen in the original transmission data, which we double-checked with an enhanced temperature resolution (see Fig.2(d)).

\[ \Delta_s \epsilon_1 = -2 \epsilon_1 (\Delta_s \omega_m/\omega_m + \Delta_s d/d) . \]  \hspace{1cm} (4)

The c-axis lattice constant does not show a kink at \( T_c \) [16] so that the spectral dependence of \( \Delta_s \epsilon_1 \) can be directly determined from \( \omega_m \)'s and fitted together with \( \Delta_s \sigma_1 \) and \( \Delta_s R \). The high-frequency \( \Delta_s \epsilon_1 \) is especially useful because it is related to the total low-frequency SW [17]

\[ \Delta_s \epsilon_1 (\omega) \approx -8 \Delta_s [A(\Omega_c) + D] \omega^{-2} \]  \hspace{1cm} (5)

(we adopt notations \( A(\omega) = \int_{-\infty}^{\omega} \sigma_1(\omega') d\omega' \) for the finite-frequency integrated SW and \( D \) for the condensate SW). As the Fabry-Perot pattern is less damped for \( x=0.12 \) due to the smaller thickness spread, the error bars of \( \Delta_s \epsilon_1 \) are much smaller in this case. We obtained a reasonably good fit of \( \Delta_s \sigma_1, \Delta_s R \) and \( \Delta_s \epsilon_1 \) simultaneously (see Fig.3), which is prerequisite for a reliable sum rule examination.

The superconductivity-driven change of \( \sigma_1 \) below \( T_c \) (detectable for \( \omega < \Omega_c \)) is governed by two factors: (i) the SC gap opening and (ii) the increase of SW above the gap. The former is much more pronounced for the OpD sample (~ 8 times larger effect). It is therefore remarkable that the latter is only 1.8-2 times smaller for the UD sample. In principle, a slight conductivity increase above the gap is expected in BCS theory in the clean limit. However, the incoherent c-axis transport is far in the dirty limit, especially in the UD regime, and calculations give a small size of this effect [18]. We propose that this is a signature of a new collective mode emerging (or sharpening) below \( T_c \). The nature of this mode is not clear at the moment. Its energy scale (100 - 270 meV) is much higher than 2∆ (~ 20-30 meV [19]). The single-layer structure seems to exclude the transverse plasmon scenario put forward for YBCO [20,21]. However there is a similarity between the effect we observe in LSCO and the increase of conductivity at the same energies in YBCO [22,20,21], so that the possibility that the phenomena in these two compounds are common in origin cannot be ruled out, even though the value of \( \sigma_1 \) as well as its absolute change below \( T_c \) is much larger in YBCO.

The occurrence of several collective modes has been recently predicted by Lee and Nagaosa [23] from a mean-field treatment of the t-J model in the SU(2) formulation. One of them, a so-called \( \phi \) gauge mode, acquires a weak c-axis spectral weight in the low-temperature orthorhombic structure due to the coupling to the buckling phonon mode. The energy scale of this mode is the in-plane exchange \( J \) (~ 100-150 meV), which agrees well with our observation. Note, that this interpretation does not involve the interplane charge transfer; the c-axis infrared activity is due to the tilting of the oxygen octahedra.

The sum rule analysis can be applied to \( \Delta_s \sigma_1 \) in the same manner as to \( \Delta \sigma_1 \). However, it directly relates to the usual FGT sum rule only close to \( T_c \) but not automatically for \( T \ll T_c \). From \( D(T) \) (see Fig.2(c)) we obtain \( \Delta_s D \) of 27 and 130 Ω\(^{-1}\)cm\(^{-2}\)K\(^{-1}\) for \( x = 0.12 \) and 0.15 respectively, denoted by the hatched area in Fig.3(a).

![FIG. 3. (a) \( \Delta_s \sigma_1 (\omega) \) (the hatched areas correspond to the condensate SW, \( \Delta_s D \)); the inset expands the higher frequency region, where transmission allows a very accurate determination of \( \Delta_s \sigma_1 (\omega) \). (b) \( \Delta_s R (\omega) \) in the phonon range. (c) \( \Delta_s \epsilon_1 (\omega) \) at high frequencies, as derived from the shift of Fabry-Perot fringes. The red and blue colors relate to \( x = 0.12 \) and 0.15 respectively. The solid curves represent the fit as described in the text.](image-url)
FIG. 4. The demonstration of the FGT sum rule violation in LSCO: (a) the relative finite-frequency SW $\Lambda_{\omega}/\Delta_sD$; (b) absolute SW $\Delta_sA(\omega)/\Delta_sD$; (c) the temperature dependence of $A(\Omega_c)$ (open circles) and $A(\Omega_c) + D$ (solid circles). $T_c$ is marked by the vertical line.

Fig 4(a) shows the relative SW $\Delta_sA(\omega)/\Delta_sD$. It saturates above $\Omega_c$ at the level of $\sim 0.2$ for $x=0.12$ and $\sim 0.7$ for $x=0.15$, thus clearly showing the presence of the FGT sum rule violation for both doping levels with relative values of almost 80% for the UD sample and 30% for the OpD sample. This is in excellent agreement with the tendency found in YBCO [6]. In contrast to the relative violation, which is stronger in the UD sample, the absolute decrease of the spectral weight $A(\Omega_c) + D$ is about 2 times larger for $x=0.15$ (Fig.4(b)). This can be also directly deduced from Fig.3(c) using formula (5). Thus the c-axis KE lowering is likely to be larger for the OpD sample, which agrees with the prediction of Ref. [8]. The positive $\Delta_s\sigma_1$ at higher frequencies significantly increases the violation, especially in the UD sample. One can even notice that the ratio between the positive part of SW above the gap for two doping levels ($~2$) is close to the ratio of $\Delta_s[A(\Omega_c) + D]$. Finally we plot the temperature dependence of $A(\Omega_c)$ and $A(\Omega_c) + D$ (Fig.4(b)). In the normal state the SW decreases with cooling down, which has to be taken into account for a proper formulation of the FGT sum rule. Below $T_c$ $A(\Omega_c)$ starts to decrease faster as a result of the gap opening, which is partially screened by the intermediate-energy increase of SW. The growth of $A(\Omega_c) + D$ in the SC state is a signature of the FGT sum rule violation.

In conclusion, our study, based on the combination of reflection and transmission spectra, reveals a detailed picture of the changes to the spectral weight in LSCO below $T_c$ for energies up to 1.8 eV. The transition to the superconducting state is accompanied not only by the gap opening at low frequencies ($2\Delta \sim 20-30$ meV) but also by the increase of $\sigma_1(\omega)$ at higher energies up to 270 meV. The latter is interpreted as a possible occurrence of a new collective mode. Its origin is not yet established. However the model by Lee and Nagaosa predicts collective modes at similar energy. The total low-frequency SW (including condensate) increases below $T_c$; the absolute value of this growth is higher in the OpD state, even though the relative FGT sum rule violation is much larger for the UD sample. Taking into account the new collective mode is decisive for a quantitative understanding of the implications of the sum-rule violation. Our results match qualitatively several findings in YBCO, thus giving a hope that many of the ‘c-axis effects’ can be understood on the same basis in different cuprates in spite of a diversity of their crystal structures. This investigation was supported by the Netherlands Foundation for Fundamental Research on Matter (FOM) with financial aid from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and by DFG via SFB 608.

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