Pairing in cuprates from high energy electronic states

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Abstract

The \textit{in-plane} optical conductivity of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ thin films with small carrier density (underdoped) up to large carrier density (overdoped) is analyzed with unprecedented accuracy. Integrating the conductivity up to increasingly higher energies points to the energy scale involved when the superfluid condensate builds up. In the underdoped sample, states extending up to 2 eV contribute to the superfluid. This anomalously large energy scale may be assigned to a change of \textit{in-plane} kinetic energy at the superconducting transition, and is compatible with an electronic pairing mechanism.

74.25.-q, 74.25.Gz, 74.72.Hs
In conventional superconductors, electrons bind into Cooper pairs by exchanging a phonon. The condensation of pairs leads to the zero-resistance superconducting state. In cuprate superconductors, the binding mechanism remains an open question. One key issue is the typical energy scale of the excitations responsible for pairing. Infrared (IR) and visible spectroscopy measures the charge density distribution as a function of energy, through the investigation of the area under the frequency \((\omega)\) and temperature \((T)\) dependent optical conductivity \(\sigma_1(\omega, T)\). This area, known as the spectral weight \(W\), is defined as:

\[
W = \int_{0+}^{\Omega_M} \sigma_1(\omega, T) d\omega
\]

where \(\Omega_M\) is a cut-off frequency. When integrating from zero to infinite frequency, this spectral weight should be conserved as it depends only on the total charge density and the bare electronic mass. Ferrell, Glover and Tinkham (FGT) noted that, in the superconducting state, the spectral weight \(\Delta W\) lost from the finite frequency (regular) conductivity is retrieved in the spectral weight \(W_s\) of the \(\delta(\omega)\) function centered at zero frequency, representing the condensate \([1]\). Actually, \(\Delta W\) is approximately equal to \(W_s\) (the so-called FGT sum rule) as soon as the cut-off frequency \(\Omega_M\) in Eq.1 covers the spectrum of excitations responsible for the pairing mechanism. In conventional superconductors, this occurs at an energy corresponding roughly to \(4\Delta\) (\(\Delta\) is the superconducting gap, related in BCS theory to the Debye frequency) \([1]\). Assuming a similar behaviour in cuprates, the FGT rule should be exhausted at \(\hbar\Omega_M \sim 0.1\) eV, as a typical maximum gap value in these d-wave superconductors is roughly 25 meV \([2]\). A violation of this sum rule, i.e. \(\Delta W < W_s\) when integrating up to 0.1 eV, was reported for the interlayer optical conductivity of some cuprate superconductors \([3–5]\), and discussed as possibly related to a change of interlayer kinetic energy. This question has indeed raised active experimental and theoretical discussions \([6–9]\), connected in particular with the interlayer tunneling theory \([10]\).

To date there is no experiment showing such unconventional behaviour directly for the in-plane conductivity of cuprates. Nevertheless this point was also given a renewed interest \([11,12]\). What is at stake is that the need of an energy scale higher than any typical phonon
energy to exhaust the FGT rule would be the hallmark of an electronic mediated pairing mechanism. Until now, the changes observed below the critical temperature $T_c$ in the in-plane optical response at large energy scales remained inconclusive [13–15].

This paper demonstrates, from a thorough study of the FGT sum rule of the in-plane conductivity, that indeed an electronic energy scale is involved when underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) becomes superconducting.

Three thin films from the Bi-2212 family were selected, at three doping levels which probe three typical locations in the phase diagram: the underdoped (UD), the optimally doped (OPD) and the overdoped (OD) regime. We find that retrieving the condensate spectral weight in the OD and OPD samples requires integrating up to an energy of the order of 0.1 eV (800 cm$^{-1}$), i.e. a conventional energy scale. In the UD sample, however, the integration must be performed up to $\sim$ 16000 cm$^{-1}$ (2 eV), an energy scale much larger than typical boson energies in a solid. The scenario which emerges hence favors an electronic pairing mechanism at low doping level.

The three films were epitaxially grown by r.f. magnetron sputtering on (100) SrTiO$_3$ substrates. The maximum critical temperature (defined at zero resistance) obtained in these conditions is $\sim$ 84 K. The OD and UD states were obtained by post-annealing the films in a controlled atmosphere [16]. X-Ray analyses confirmed that the films are single phase. Our films have the following characteristics: i) UD film: $T_c = 70$ K, thickness $\sim$ 2400 Å; ii) nearly–optimally doped (OPD) film: $T_c = 80$ K, thickness $\sim$ 4400 Å; iii) OD film: $T_c = 63$ K, thickness $\sim$ 3000 Å. Their optical homogeneity was verified by infrared microscopy with a lateral resolution of 20 $\mu$m [17]. The reflectivities, taken at 15 temperatures between 300 K and 10 K, were measured in the spectral range [30 – 7000] cm$^{-1}$ with a Fourier Transform spectrometer, supplemented with standard visible spectroscopy in the range [4000 – 25000] cm$^{-1}$. Using thin films rather than single crystals allows to measure reliably relative variations in reflectivity within less than 0.2 %, due to their large surface (typically 6 x 6 mm$^2$).

It is known that temperature changes of the optical response in the mid-infrared and
the visible ranges are small, but cannot be neglected \[18\]. Yet, most studies rely on a single spectrum at one temperature in the visible range \[15\]. We did monitor the temperature evolution of the reflectivity spectra in the full available range. This is obviously important if one is looking for a spectral weight transfer originating from (or going to) any part of the whole frequency range.

The contribution of the substrate to the experimentally measured reflectivities precludes the Kramers-Kronig analysis in thin films. For all raw spectra, an accurate fitting (within \( \leq 0.5 \% \)), taking into account the substrate response at each measured temperature and the interference pattern in the film, was performed (Fig.1, top panel) \[17,19\]. This procedure determines the dielectric function for Bi-2212, hence the optical conductivity. Moreover, the fit yields a valuable extrapolation of the conductivity in the low energy range (\( \omega < 30 \text{ cm}^{-1} \), not available experimentally) \[20\], which is important in the evaluation of the spectral weight.

The conductivities at \( T_A \geq T_c \) and \( T_B < T_c \), are shown in Fig. 1 (lower panel), up to 800 \( \text{cm}^{-1} \) (0.1 eV) for the UD (\( T_A = 80 \text{ K} \)) and OD (\( T_A = 70 \text{ K} \)) samples respectively. In both cases, \( T_B = 10 \text{ K} \). In the OD sample, the curve \( \sigma_1(\omega, T \leq T_c) \) lies below the one at \( T \geq T_c \), exhibiting an expected loss of spectral weight in this energy range. In contrast, the curve \( \sigma_1(\omega, T \leq T_c) \) for the UD sample lies above the one at \( T \geq T_c \), up to 100 \( \text{cm}^{-1} \), then crosses it, and no loss of spectral weight is apparent in the energy range shown.

From an experimental point of view, the FGT sum rule usually compares the change \( \Delta W = W(T_A) - W(T_B) \) (Eq.1) and the superfluid spectral weight \( W_s \). \( W_s \) was determined for \( T < T_c \) at low frequencies within the measured spectral range, by looking at the region where the real part of the dielectric function \( \varepsilon_1(\omega) \) behaves linearly when plotted versus \( 1/\omega^2 \) (London approximation). An example is shown in the inset of Fig.1. The slope is directly related the superfluid spectral weight \( W_s \) through the “London” frequency \( \Omega_L = c/\lambda_L \), where \( \lambda_L \) is the London penetration depth. At 10 K, for instance, we find \( \Omega_L = 7200 \text{ cm}^{-1} \) and 2350 \( \text{cm}^{-1} \) for the OD and UD samples respectively \[21\].

Figure 2 shows the ratio \( \Delta W/W_s \) for the samples studied in this work. Note that the figure extends actually over three different energy scales. For the OD and OPD samples, the
sum rule is exhausted at roughly 500 − 1000 cm\(^{-1}\), i.e., 2.5 to 5 times the maximum gap, as in conventional superconductors. In the UD sample though, \(\Delta W/W_s\) starts negative and becomes positive at \(\sim 600\) cm\(^{-1}\). Even at energies as large as 8000 cm\(^{-1}\), \(\Delta W/W_s\) \(\sim 0.7\). It keeps increasing with increasing energy and approaches 1 at \(\sim 16000\) cm\(^{-1}\). A large part (\(\sim 30\%\)) of the superfluid weight in the underdoped regime thus builds up at the expense of spectral weight coming from high energy regions of the optical spectrum \((\hbar \omega \geq 1\text{eV})\).

This remarkable behavior must be critically examined in light of the uncertainties that enter in the determination of the ratio \(\Delta W/W_s\). Firstly, the determination of \(\Delta W\) assumes that \(W(T_A)\) is a fair estimate of the normal state regular spectral weight \(W_n(T_B)\), if one could drive the system normal below \(T_c\). While this assumption is correct in BCS superconductors, it is no longer valid for High-\(T_c\) superconductors \[8\], hence our taking the normal-state spectral weight \(W(T_A \geq T_c)\) instead of \(W_n(T_B)\) (unknown) may bias the sum rule. The error incurred by doing so can be estimated as follows. Figure 3 displays the temperature dependence, from 300 K down to 10 K, of the relative spectral weight \(W(\Omega_M, T)/W(\Omega_M, 300\text{ K})\), for three selected integration ranges, according to Eq.1. At \(\Omega_M=1000\) cm\(^{-1}\), the normalized spectral weight exhibits a significant increase as the temperature is lowered, and could therefore keep changing in the superconducting state. One could infer an increase of \(\sim 10\%\) of this relative spectral weight for both samples if assuming a linear extrapolation of the data. Hence \(W(T_A)\) is most likely to give too small an estimate for \(W_n(T_B)\) at \(T < T_c\), in this energy range. To get a better insight of this possible underestimate, the superfluid weight \(W_s(T)\) was added to the spectral weight \(W(T_B)\) (open symbols in Fig. 3), at a frequency \(\omega = \Omega_M\) and a temperature \(T < T_c\). The points extrapolate reasonably well the high temperature data, thus suggesting an upper bound for the error \[22\]. These estimates have been performed for a number of cut-off frequencies starting from 100 cm\(^{-1}\) (the error increases at low frequency). At 5000 cm\(^{-1}\) and above, relying on similar considerations about the temperature evolution of the relative spectral weights shown in Fig.3, the changes with temperature of the normal state spectral weight should be approximately 10 times smaller than at 1000 cm\(^{-1}\). Note that at 20000 cm\(^{-1}\), the spectral weight is constant, meaning that the
relevant energy scale for the FGT sum rule has been achieved. Therefore, above 5000 cm$^{-1}$, the uncertainty in $W_n(T_B)$ becomes negligible compared to those due to the error in the relative change with temperature (the error in the absolute value being irrelevant), in the fitting, and in the determination of $W_s$.

The three latter uncertainties were calculated self-consistently since the error in the determination of the superfluid density is related to the error in the determination of the optical conductivity. They yield an upper bound of 15% – 20% in the uncertainty on the evaluation of $\Delta W/W_s$, for all frequencies. All uncertainties can then be incorporated in the analysis of the ratio $\Delta W/W_s$, and are represented by the error bars in Fig. 3. Therefore, the top of the error bars delineates the upper limit for the FGT sum rule at each frequency.

For the UD sample, it is then clear that the negative value could be assigned to an incorrect estimate of $W_n$. However, the violation of the sum rule for this sample, with $\Delta W/W_s = 0.65 \pm 0.18$ at 8000 cm$^{-1}$ is also clearly established. Within the error bars, the sum rule is exhausted in this sample above 16000 cm$^{-1}$. Underdoped Y-123 showed a more conventional behavior, possibly because, as suggested, only one spectrum is usually recorded in the visible range which is precisely the energy range which matters in this case \[15\]. Our results for the OD and OPD samples agree with earlier similar work in YBa$_2$Cu$_3$O$_{7-\delta}$ (Y-123) and Tl$_2$Ba$_2$CuO$_{6+\delta}$ (Tl-2212) \[3\].

In the context of the tight-binding Hubbard model, a relation exists between the low-frequency spectral weight and the kinetic energy $E_{kin}$ per copper site \[15\]:

$$\frac{\Delta W}{W_s} = \frac{4\pi c}{137\hbar V \Omega_L^2} \left( E_{kin,s} - E_{kin,n} \right) = 1$$

where $c$ is the (average) lattice spacing in the plane, $V$ is the volume per site (SI units). This relation means that a breakdown of the FGT sum-rule up to an energy $\hbar \Omega_M$ of the order of the plasma frequency ($\sim 1$ eV for Bi-2212) is related to a change in the carrier kinetic energy $\Delta E_k = E_{kin,s} - E_{kin,n}$, when entering the superconducting state. According to our results in the UD sample (Fig.2), $\Delta W/W_s = 0.65 \pm 0.18$ at 1 eV, which yields $\Delta E_k = 1.1 \pm 0.3$ meV per copper site. This would be a huge kinetic energy gain, $\sim 15$
times larger than the condensation energy $U_0$. For (optimally) doped Bi-2212, $U_0 \simeq 1 \text{ J/g-at} \approx 0.08 \text{ meV per copper site}$. A change of the in-plane kinetic energy could actually drive the superconducting transition, as it has been proposed in various scenarios: holes moving in an antiferromagnetic background, interlayer tunneling theory, or hole undressing. The latter scenario suggests that the violation of the FGT sum rule must be more conspicuous for a dilute concentration of carriers and that, upon doping, a conventional energy scale exhausting the FGT sum-rule should be retrieved. Also, the kinetic energy lowering $\Delta E_k$ may be much larger than the condensation energy, and was estimated for Tl-2212 to be $\sim 1 - 3 \text{ meV per planar oxygen}$, which results into $0.5 - 1.5 \text{ meV per copper site}$. It was also suggested that it should be easier to observe the sum rule violation in UD samples in the dirty limit, which could apply in our case.

Recently, STM experiments in optimally doped Bi-2212 samples showed small scale spatial inhomogeneities, over $\simeq 14 \text{ Å}$, which are reduced significantly when doping increases, and whose origin could be local variations of oxygen concentration. Since the wavelength in the full spectral range is larger than 14 Å, the reflectivity performs a large scale average of such an inhomogeneous medium. The implications in the conductivity are still to be investigated in detail, but it is presently unclear how this could affect the sum rule.

In conclusion, we have have found for the in-plane conductivity of the underdoped Bi-2212 a clear violation of the sum rule at 1 eV, corresponding to a kinetic energy lowering (within the framework of the tight-binding Hubbard model) of $\sim 1 \text{ meV per copper site}$. The very large energy scale required in order to exhaust the sum rule in the UD sample cannot be related to a conventional bosonic scale, hence strongly suggests an electronic pairing mechanism.

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FIGURES

FIG. 1. Top panel: measured reflectivity spectra of the underdoped sample at 250 K and 10 K (open circles). Three peaks from the SrTiO$_3$ substrate are visible at 60, 180 and 530 cm$^{-1}$. The solid lines are the fitted spectra. Bottom panel: real part of the calculated conductivity at temperatures above $T_c$ at 80 K (open diamonds) and 70 K (open circles) and at 10 K (full symbols) for the UD (right scale) and OD (left scale) samples respectively. The conductivities are extrapolated from 30 cm$^{-1}$ down to zero as a result of the fit. Inset: linear fit (solid line) of the low frequency $\varepsilon_1(\omega, T < T_c)$ data from the UD sample (open squares), versus $\omega^{-2}$.

FIG. 2. Ratio $\Delta W/W_s$ versus frequency showing the exhaustion of the FGT sum rule at conventional energies for the OD (diamonds, right error bars) and OPD (triangles, middle error bars) samples. An unconventional ($\sim 16000$ cm$^{-1}$ or 2 eV) energy scale is required for the UD sample (circles, left error bars). Note that the frequency scale changes at 800 and 8000 cm$^{-1}$.

FIG. 3. Effective spectral weight $W(T, \Omega_M)/W(300 \ K, \Omega_M)$ versus temperature for the underdoped (top panel) and overdoped (bottom panel) samples, at different cutoff frequencies $\Omega_M$ (full symbols). $\Omega_M = 1000$ cm$^{-1}$ (circles), 5000 cm$^{-1}$ (up triangles), and 20000 cm$^{-1}$ (down triangles). Open symbols are obtained by adding the superfluid weight $W_s(T)$ to the spectral weight $W(T < T_c)$. 

\[ \sigma_1(T) \left( 10^3 \, \Omega^{-1} \cdot \text{cm}^{-1} \right) \]

\[ \varepsilon_1 \left( 10^3 \right) \]

Reflectivity

Wavenumber (cm\(^{-1}\))

UD
10K
250K
