Sum rules and energy scales in the high-temperature superconductor YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6+\textgamma

C. C. Homes* and S. V. Dordevic

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

D. A. Bonn, Ruixing Liang, and W. N. Hardy

Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

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The Ferrell-Glover-Tinkham (FGT) sum rule has been applied to the temperature dependence of the in-plane optical conductivity of optimally-doped YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6.95} and underdoped YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{6.60}. Within the accuracy of the experiment, the sum rule is obeyed in both materials. However, the energy scale \( \omega_c \) required to recover the full strength of the superfluid \( \rho_s \) in the two materials is dramatically different; \( \omega_c \approx 800 \text{ cm}^{-1} \) in the optimally doped system (close to twice the maximum of the superconducting gap, \( 2\Delta_0 \)), but \( \omega_c \gtrsim 5000 \text{ cm}^{-1} \) in the underdoped system. In both materials, the normal-state scattering rate close to the critical temperature is small, \( \Gamma < 2\Delta_0 \), so that the materials are not in the dirty limit and the relevant energy scale for \( \rho_s \) in a BCS material should be twice the energy gap. The FGT sum rule in the optimally-doped material suggests that the majority of the spectral weight of the condensate comes from energies below \( 2\Delta_0 \), which is consistent with a BCS material in which the condensate originates from a Fermi liquid normal state. In the underdoped material the larger energy scale may be a result of the non-Fermi liquid nature of the normal state. The dramatically different energy scales suggest that the nature of the normal state creates specific conditions for observing the different aspects of what is presumably a central mechanism for superconductivity in these materials.

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I. INTRODUCTION

Sum rules and conservation laws play an important role in physics. In spectroscopy, the conductivity sum rule is particularly useful and is an expression of the conservation of charge.\textsuperscript{1} In metallic systems, the conductivity sum rule usually yields the classical plasma frequency or the effective number of carriers. In superconductors, below the critical temperature \( T_c \), some fraction of the carriers collapse into the \( \delta(\omega) \) function at zero frequency that determines the London penetration depth \( \lambda_L \), with a commensurate loss of spectral weight from low frequencies (below twice the superconducting energy gap, \( 2\Delta_0 \)). This shift in spectral weight may be quantified by the application of the conductivity sum rule to the normal and superconducting states, as discussed by Ferrell, Glover and Tinkham (the FGT sum rule),\textsuperscript{3,4} which is used to estimate the strength of the superconducting condensate \( \rho_s = c^2/\lambda_L^2 \). The theory of superconductivity described by Bardeen, Cooper and Schrieffer (BCS) holds that while the kinetic energy of the superconducting state is greater than that of the normal state,\textsuperscript{4,5} this increase is compensated by the reduction in potential energy which drives the transition (the net reduction of energy is simply the condensation energy). However, it has been proposed that in certain hole-doped materials the superconductivity could arise from a lowering of the kinetic rather than the potential energy.\textsuperscript{6} In such a system non-local transfers of spectral weight would result in the apparent violation of the FGT sum rule, which would yield a value for the strength of \( \rho_s \) that would be too small (\( \lambda_L \) would be too large).\textsuperscript{5–8} Similar models in the cuprate materials propose either strong coupling,\textsuperscript{9,10} or that the normal state is not a Fermi liquid and that superconductivity is driven either by the recovery of frustrated kinetic energy when pairs are formed,\textsuperscript{11,12} by lowering the in-plane zero-point kinetic energy,\textsuperscript{13} or by the condensation of preformed pairs.\textsuperscript{14}

Experimental results along the poorly-conducting in-plane (\( c \)-axis) direction in several different cuprate materials support the view that the kinetic energy is reduced below the superconducting transition.\textsuperscript{15–17} In some materials, the low-frequency \( c \)-axis spectral weight accounts for only half of the strength of the condensate. However, this violation of the FGT sum rule appears to be restricted to the underdoped materials which display a pseudogap in the conductivity.\textsuperscript{18} The dramatically lower value of the strength of the condensate along the \( c \) axis makes it easier to observe kinetic energy contributions. In comparison, the much larger value of the condensate in the copper-oxygen planes makes it much more difficult to observe changes due to the kinetic energy based on optical sum rules.\textsuperscript{19,20} Recently, high-precision measurements in the near-infrared and visible region have reported small changes in the in-plane spectral weight associated with the onset of superconductivity, supporting the argument that changes in the kinetic energy are indeed occurring.\textsuperscript{21–23} While the relatively small changes of the in-plane spectral weight make it difficult to make statements about the kinetic energy, it is nonetheless a strong motivation to examine the evolution of the spectral weight in detail to see if there are unexpected signatures of an unconventional mechanism for the superconductivity in this class of materials.

In this paper we examine the changes of the in-plane
spectral weight and the evolution of the superconducting condensate in the optimally doped and underdoped detwinned YBa$_2$Cu$_3$O$_{6+x}$ single crystals for light polarized perpendicular to the copper-oxygen chains, along the $a$ axis. The BCS model requires that the spectral weight of the condensate be fully formed at energies comparable to the energy gap ($\omega_c \approx 2\Delta$), with no subsequent violation of the FGT sum rule. This is precisely what is observed for the optimally-doped material, within the limits of experimental accuracy for the sum rules, which is estimated to be about 5%. However, in the underdoped material only 80% of the spectral weight of the condensate has been recovered at energies comparable to $2\Delta$; the FGT sum rule must be extended to considerably higher frequencies to recover the remaining spectral weight ($\omega_c \gtrsim 0.6$ eV). For $T \gtrsim T_c$, the normal-state scattering rate is determined to be small, so this shift in spectral weight cannot be attributed to dirty-limit effects in response to impurities. However, the nature of the normal state is dramatically different in the optimally-doped material, which is reminiscent of a Fermi liquid, and the underdoped material, which develops a pseudogap and displays non-Fermi liquid behavior. The dramatically different energy scales required to recover the full value of $\rho_s$ suggest that these aspects of the superconductivity are related to the normal state properties from which it emerges.

II. Experiment and Sample Preparation

Details of the growth and characterization of the mechanically-detwinned YBa$_2$Cu$_3$O$_{6+x}$ crystals have been previously described in detail$^{24,25}$ and will be discussed only briefly. The crystal had a small amount of Ni deliberately introduced, Cu$_{1-x}$Ni$_x$, where $x = 0.0075$. Such a small concentration of Ni results in a critical temperature which is slightly lower ($\sim 2$ K) than the pure materials, with a somewhat broader transition. The same detwinned crystal has been carefully annealed to produce two different oxygen concentrations, $x = 0.95$ ($T_c \approx 91$ K) and 0.60 ($T_c \approx 57$ K). The reflectance for light polarized along the $a$ axis (perpendicular to the CuO chains, therefore probing only the CuO$_2$ planes) has been measured at a variety of temperatures over a wide frequency range ($\approx 40$ to 9000 cm$^{-1}$) using an overfilling technique; this reflectance has been extended to very high frequency ($3.5 \times 10^9$ cm$^{-1}$) using the data of Basov et al.$^{27,28}$ and Romberg et al.$^{29}$ The absolute value of the reflectance is estimated to be accurate to within 0.2%. The optical properties are calculated from a Kramers-Kronig analysis of the reflectance. The optical conductivity, which dealt with the effects of Ni doping on the CuO chains and the reduction of the in-plane anisotropy, has been previously reported.$^{30}$ The presence of Ni in such small concentrations was not observed to have any effect on the conductivity of the CuO$_2$ planes in either the normal or superconducting states.

III. Results and Discussion

A. Optical sum rules

Optical sum rules comprise a powerful set of tools to study and characterize the lattice vibrations and electronic properties of solids. The spectral weight may be estimated by a partial sum rule of the conductivity$^{1,31}$

$$N(\omega_c) = \frac{120}{\pi} \int_{0}^{\omega_c} \sigma(\omega) d\omega \rightarrow \omega_c^2$$

where $\omega_c^2 = 4\pi n e^2 / m_0$ is the classical plasma frequency, $n$ is the carrier concentration, and $m_0$ is the bare optical mass. In the absence of bound excitations, this expression is exact in the limit of $\omega_c \rightarrow \infty$. However, any realistic experiment involves choosing a low-frequency cutoff $\omega_c$. When applied to the Drude model

$$\tilde{\epsilon}(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\Gamma)},$$

where $\epsilon_{\infty}$ is the contribution from the ionic cores, and $\Gamma = 1/\tau$ is the scattering rate, the conductivity sum rule indicates that 90% of the spectral weight is recovered for $\omega_c \sim 6\Gamma$. For even modest choices of $\Gamma$, $\omega_c$ can be quite large ($\sim \omega_p$). This places some useful constraints on the confidence limits for the conductivity sum rule in the normal state.

The conductivity in the superconducting state for any polarization $\mathbf{r}$ has two components$^9$

$$\sigma_{1,\mathbf{r}}^{SC}(\omega) = \frac{\pi}{120} \rho_{s,\mathbf{r}} \delta(\omega) + \sigma_{1,\mathbf{r}}^{reg}(\omega).$$

The first part is associated with the superconducting $\delta(\omega)$ function at zero frequency, where $\rho_{s,\mathbf{r}}$ is the superfluid stiffness, or strength of the superconducting order.$^{32}$ This is often expressed as the square of a plasma frequency $\omega_{pS}^2 = 4\pi n_s e^2 / m_s^*$, where $n_s$ is the density of superconducting electrons, and $m_s^*$ is the effective mass tensor. The second component $\sigma_{1,\mathbf{r}}^{reg}(\omega)$ is referred to as the “regular” component for $\omega > 0$ and is associated with the unpaired charge carriers.

A variation of the conductivity sum rule in a superconductor is to study the amount of spectral weight that collapses into the superconducting $\delta(\omega)$ function at the origin below the critical temperature.$^5$ This scenario is represented in Fig. 1, which shows the normalized conductivity for a BCS $s$-wave model for an arbitrary purity level$^{33}$ where the scattering rate in the normal state is chosen as $\Gamma = 2\Delta$ ($2\Delta$ is the full gap value for $T \ll T_c$). The solid line shows the real part of the optical conductivity $\sigma_1(\omega)$ in the normal state for $T \gtrsim T_c$, while the dashed line is the calculated value for $\sigma_1(\omega)$ in the superconducting state for $T \ll T_c$. For $T \ll T_c$ the gap is
determined in a low-frequency limit, which removes the \( \rho \) thus probes just the superfluid response, and (ii) \( \omega < 2\Delta \), above which the onset of absorption occurs. The missing spectral weight represented by the hatched area represents the strength of the condensate \( \omega_{PS}^2 \). This area may be estimated by the FGT sum rule\(^3\,^3\):

\[
\omega_{PS}^2 = \frac{120}{\pi} \int_{0+}^{\omega_c} \left[ \sigma_{1,n}(\omega) - \sigma_{1,s}(\omega) \right] d\omega. \tag{4}
\]

where \( \sigma_{1,n}(\omega) \equiv \sigma_1(\omega, T \gtrsim T_c) \) and \( \sigma_{1,s}(\omega) \equiv \sigma_1(\omega, T \ll T_c) \). An alternative method for extracting the superfluid density relies on only the real part of the dielectric function. Simply put, if upon entering the superconducting state for \( T \ll T_c \) it is assumed that all of the carriers collapse into the condensate, then \( \omega_{PS} \equiv \omega_p \) and \( \Gamma \to 0 \), so that the function of the form of the dielectric function in Eq. (2) becomes \( \epsilon_1(\omega) = \epsilon_\infty - \omega_{PS}^2/\omega^2 \); in the limit of \( \omega \to 0 \), \( \rho_s \propto \omega_{PS}^2 = -\omega^2\epsilon_1(\omega) \). This is a generic result in response to the formation of a \( \delta(\omega) \) function and is not model dependent. The value for \( -\omega^2\epsilon_1(\omega) \) is shown in Fig. 2 for \( \Gamma = 2\Delta \). There is a small dip near \( 2\Delta \) (which becomes somewhat washed out for \( \Gamma \gg 2\Delta \)), and the curve converges cleanly in the \( \omega \to 0 \) limit. The determination of \( \rho_s \) from \( -\omega^2\epsilon_1(\omega) \) has two main advantages: (i) it relies only on the value of \( \epsilon_1(\omega) \) for \( T \ll T_c \) and thus probes just the superfluid response, and (ii) \( \rho_s \) is determined in a low-frequency limit, which removes the uncertainty of the high-frequency cut-off frequency \( \omega_c \). The conductivity in the normal state \( \sigma \) for a BCS model for a normal-state scattering rate of \( \Gamma = 2\Delta \). The conductivity in the normal state for \( T \ll T_c \) is shown by the solid line (normalized to unity), while the conductivity in the superconducting state \( \sigma(\omega, T \ll T_c) \) is shown by the dashed line. For \( T \ll T_c \), the superconducting gap \( 2\Delta \) is fully formed and there is no absorption below this energy. The hatched area illustrates the spectral weight that has collapsed into the superconducting \( \delta(\omega) \) function at the origin.

FIG. 1: The real part of the optical conductivity calculated for a BCS model for a normal-state scattering rate of \( \Gamma = 2\Delta \). The conductivity in the normal state \( \sigma(\omega, T \gtrsim T_c) \) is shown by the solid line (normalized to unity), while the conductivity in the superconducting state \( \sigma(\omega, T \ll T_c) \) is shown by the dashed line. For \( T \ll T_c \), the superconducting gap \( 2\Delta \) is fully formed and there is no absorption below this energy. The hatched area illustrates the spectral weight that has collapsed into the superconducting \( \delta(\omega) \) function at the origin.

FIG. 2: The value of \( -\omega^2\epsilon_1(\omega) \) calculated from the BCS model for \( T \ll T_c \) for the normal-state scattering rate \( \Gamma = 2\Delta \) (solid line); \( \rho_s = -\omega^2\epsilon_1(\omega) \) in the limit of \( \omega \to 0 \). Note that there is also a small minima near \( 2\Delta \) (long dashed line).

The rapidity with which the spectral weight of the condensate is captured by the Ferrell-Glover-Tinkham sum rule is shown in Fig. 3 for three different choices of the normal-state scattering rate relative to the superconducting energy gap. Here the solid line is the conductivity sum rule applied to \( \sigma_1(\omega) \) in the normal state \( (T \gtrsim T_c) \), effectively \( \omega_p^2 \), while the dotted line is the conductivity sum rule for \( T \ll T_c \), which yields \( \omega_p^2 - \omega_{PS}^2 \). The difference between the two curves is the dashed line, which is simply \( \omega_{PS}^2 \). To simplify matters, in each case the integrals have been normalized with respect to the strength of the fully-formed condensate \( \rho_s \), to yield a dimensionless ratio. In Fig. 3(a) the normal state scattering rate has been chosen to be \( \Gamma = \Delta/2 \) (“clean limit”). It may be observed that nearly all of the spectral weight in the normal state collapses into the condensate. Furthermore, the condensate is essentially fully-formed above \( 2\Delta \). In Fig. 3(b) the normal state scattering rate has been chosen to have an intermediate value \( \Gamma = 2\Delta \) (the situation depicted in Fig. 1). The larger value of \( \Gamma \) has the effect of shifting more of the normal-state spectral weight above \( 2\Delta \), which reduces the strength of the condensate. However, despite the larger value for \( \Gamma \) and the reduced strength of the condensate, it is once again almost fully-
The temperature dependence of the optical conductivity of optimally-doped YBa$_2$Cu$_3$O$_{6.95}$ ($T_c \approx 91$ K) for light polarized along the $a$ axis is shown in Fig. 4(a). The Drude-like low-frequency conductivity narrows as the temperature decreases from room temperature to just above $T_c$; well below the superconducting transition the low-frequency conductivity has decreased and the missing spectral weight has collapsed into the condensate. However, an optical gap is not observed and there is a great deal of residual conductivity at low frequency. The conductivity can be reasonably well described using a "two-component" model, with a Drude component and a number of bound excitations, usually Lorentz oscillators. While the low-frequency conductivity is satisfactorily described by a Drude term, the midinfrared region is not and a large number of oscillators are required to reproduce the conductivity. For this reason, a generalized form of the Drude model is often adopted where the scattering rate is allowed to have a frequency dependence (in order to preserve the Kramers-Kronig relation, the effective mass must then also have a frequency dependence). The frequency-dependent scattering rate has the form

$$\frac{1}{\tau_{\omega}} = \frac{\omega_{p,a}^2}{4\pi} \text{Re} \left[ \frac{1}{\sigma(\omega)} \right]. \quad (5)$$

The value for the plasma frequency used to scale the expression in Eq. (5) has been estimated using the conductivity sum rule for $\sigma_{1,a}(\omega, T \approx T_c)$, using $\omega_c \approx 1$ eV, which yields a value for $\omega_{p,a} \approx 16700$ cm$^{-1}$, or about 2 eV (Ref. 30). The frequency-dependent scattering rate $1/\tau_{\omega}(\omega)$ is shown in the inset of Fig. 4(a), and in the normal state shows a monotonic increase with frequency, and an overall downward shift with decreasing temperature. Below $T_c$, there is a strong suppression of $1/\tau_{\omega}(\omega)$ at low frequency associated with the formation of the superconducting gap, with a slight overshoot and then the recovery of the normal-state value at high-frequency.

This behavior is characteristic of optimally-doped and overdoped materials.

The behavior of the oxygen-underdoped material YBa$_2$Cu$_3$O$_{6.60}$ ($T_c \approx 57$ K) for light polarized along the $a$ axis, shown in Fig. 4(b), shows some significant differences from the optimally-doped material. The Drude-like conductivity at room temperature is extremely broad. However, at $T \approx T_c$, the Drude-like conductivity has narrowed dramatically, and there has been a significant shift of spectral weight to low frequencies. For $T \ll T_c$, the low frequency conductivity has decreased, indicating the formation of a condensate. However, the effect is not as dramatic as it was in the optimally-doped material, indicating that the strength of the condensate is not as great. Once again, there is a considerable amount of residual conductivity at low frequency for $T \ll T_c$. The frequency-dependent scattering rate is shown in the inset, along with the estimated value of $\omega_{p,a} \approx 13250$ cm$^{-1}$.
FIG. 4: The optical conductivity of (a) optimally-doped YBa$_2$Cu$_3$O$_{6.95}$, and (b) underdoped YBa$_2$Cu$_3$O$_{6.60}$ at room temperature (solid line), $T \gg T_c$ (dotted line), and $T \ll T_c$ (dashed line) for light polarized along the $a$ axis. The inset in each panel shows the frequency dependent scattering rate and the estimated value of $\omega_{pa}$. The Drude-like conductivity of the optimally-doped material narrows somewhat in the normal state but the scattering rate shows no indication of a pseudogap; below $T_c$, a considerable amount of spectral weight collapses into the condensate. In the underdoped material, the conductivity narrows considerably in the normal state and the scattering rate indicates the opening of a pseudogap; the condensation is less dramatic than in the optimally-doped case.

estimated from the conductivity sum rule. As the temperature decreases in the normal state $1/\tau_a(\omega)$ decreases rapidly at low frequency, which is taken to be evidence for the formation of a pseudogap. The large drop in the normal-state scattering rate for $1/\tau_a(\omega \rightarrow 0)$ is a reflection of the dramatic narrowing of the conductivity and is an indication that the reduced doping has not created a large amount of scattering due to disorder — on this basis, the system is not in the dirty limit.

The superfluid density $\rho_{s,a}$ has been estimated from the response of $-\omega^2 \epsilon_{1,a}(\omega)$ in the zero-frequency limit for $T \ll T_c$ for the optimally and underdoped materials, shown in Fig. 5. The estimate of $\rho_{s,a}$ assumes that the response of $\epsilon_{1,a}(\omega)$ at low frequency is dominated by the condensate, but it has been shown that along the $c$ axis, there is enough residual conductivity to affect $\epsilon_{1,c}(\omega)$ and thus the values of $\rho_{s,c}$, typically resulting in an overestimate of the strength of the condensate. The presence of residual conductivity for $T \ll T_c$ suggests that $\rho_{s,a}$ may be overestimated in this case as well. However, as we noted earlier, the real part of the conductivity in the superconducting state may be expressed as a regular part due to unpaired carriers, and a $\delta(\omega)$ function at zero frequency; the response of $\epsilon_{2,a}(\omega)$ is limited to the $\delta(\omega)$ function, which is zero elsewhere. However, $\epsilon_{2,a}(\omega)$ has been determined experimentally to be non-zero: if we refer to this as $\epsilon_{2,a}^{reg}(\omega)$, then $\epsilon_{1,a}^{reg}(\omega)$ may be determined through the Kramers-Kronig relation, and the superfluid density estimated as

$$\rho_{s,a}(\omega) = \omega^2 \left[ \epsilon_{1,a}^{SC}(\omega) - \epsilon_{1,a}^{reg}(\omega) \right],$$

FIG. 5: The function $-\omega^2 \epsilon_{1,a}(\omega)$ vs frequency for optimally doped YBa$_2$Cu$_3$O$_{6.95}$ (solid line) and underdoped YBa$_2$Cu$_3$O$_{6.60}$ (dashed line) along the $a$ axis at $\approx 10$ K ($T \ll T_c$). The superfluid density is $\rho_{s,a} = -\omega^2 \epsilon_{1,a}(\omega \rightarrow 0)$; taking the squares to render the units the same as those of a plasma frequency yields $\sqrt{\rho_{s,a}} = 8670 \pm 90$ cm$^{-1}$ and $\sqrt{\rho_{s,a}} = 5620 \pm 60$ cm$^{-1}$ for the optimally and underdoped materials, respectively. Note also that in both materials there is a slight suppression of $\omega^2 \epsilon_{1,a}(\omega)$ in the $500 - 700$ cm$^{-1}$ region, close to the estimated value of $2\Delta_o$. 

$\rho_{s,a}(\omega) = 5620$ cm$^{-1}$
a slight suppression of $-\omega^2\tau_1(\omega)$ in the 500−700 cm$^{-1}$ region, which is in agreement with estimates for the superconducting gap maximum $2\Delta_0 \approx 500$ cm$^{-1}$ (adopting the notation for a $d$-wave superconductor) in overdoped YBa$_2$Cu$_3$O$_{6.95}$ (Ref. 41). Studies of other cuprate systems suggest that the gap maximum increases with decreasing doping, despite the reduction of $T_c$. The integrated values of the conductivity in the normal ($T \gtrsim T_c$) and superconducting ($T \ll T_c$) states are indicated by the solid $[N_n(\omega)]$ and dashed $[N_s(\omega)]$ lines for YBa$_2$Cu$_3$O$_{6.95}$ and YBa$_2$Cu$_3$O$_{6.60}$ along the $a$ axis in the upper and lower panels of Fig. 6, respectively. For YBa$_2$Cu$_3$O$_{6.95}$, $N_n(\omega)$ increases rapidly with frequency, but does not display any unusual structure. On the other hand, $N_s(\omega)$ evolves more slowly, and has several inflection points at low frequency which are thought to be related to the peaks in the electron-boson spectral function. The difference between the two curves $\omega_{ps}^2 = N_n(\omega) - N_s(\omega)$ is shown by the dashed line in Fig. 6(a). This quantity increases quickly and then saturates above $\approx 800$ cm$^{-1}$ to a constant value. This plot is reminiscent of the BCS material with moderate scattering, discussed in Fig. 3(b). The sum rules applied to YBa$_2$Cu$_3$O$_{6.60}$ shown in Fig. 6(b) are similar to the optimally-doped case. However, the overall magnitude has decreased, a reflection of the decreased carrier concentration within the copper-oxygen planes in the underdoped material. While the condensate is also lower, it now appears that it does not saturate as quickly as was the case in the optimally-doped material.

A more detailed examination of the evolution of the weight of the condensate for YBa$_2$Cu$_3$O$_{6.95}$ (solid line) and YBa$_2$Cu$_3$O$_{6.60}$ (dotted line), normalized to the values of $\rho_{s,a}$ determined in Fig. 5, is shown in Fig. 7. The error associated with the FGT sum rule has been determined in the following way. The optical conductivity has been calculated for $R(\omega,T) \pm 0.1\%$ for $T \gtrsim T_c$ and $T \ll T_c$, the normal and superconducting states, respectively. The FGT sum rule is then applied to the resulting high and low values for the conductivity, and the error limits are taken as the deviation from the curve.

FIG. 6: The conductivity sum rules applied to (a) optimally-doped YBa$_2$Cu$_3$O$_{6.95}$ and (b) underdoped YBa$_2$Cu$_3$O$_{6.60}$ for light polarized along the $a$ axis for $T \gtrsim T_c$ [as in Fig. 5(a)] and for $T \ll T_c$ [as in Fig. 5(b)]. The integrated values of the conductivity in the normal and superconducting states are indicated by the solid lines $[N_n(\omega)]$ and dashed lines $[N_s(\omega)]$, respectively. The conductivity sum rules are then applied to the values of $\rho_{s,a}$ determined in Fig. 5. The curves describing the condensate have been normalized to the values of $\rho_{s,a}$ shown in Fig. 5. The condensate for the optimally-doped material has saturated by $\approx 800$ cm$^{-1}$, while in the underdoped material the condensate is roughly 80% formed by this frequency, but the other 20% is not recovered until much higher frequencies. The error bars on the curve for the underdoped material indicate the uncertainty associated with the FGT sum rule. Inset: The low-frequency region.
generated simply from $R(\omega, T)$, which are estimated to be about ±3%. It should be noted that most of the uncertainty is introduced when the reflectance is close to unity, as $\sigma_1 \propto 1/(1 - R)$ and even small uncertainties in the reflectance can lead to large errors in the optical conductivity. When the FGT sum rule is exhausted, the ratio is unity by definition. For the optimally-doped material, this occurs rapidly and 90% of the spectral weight in the has been recovered by about 500 cm$^{-1}$, and the ratio approaches unity at $\omega_c \approx 800$ cm$^{-1}$, and remains constant even out to very high frequencies (over 0.5 eV). This rapid formation of the condensate has also been observed in the optimally-doped materials$^{45,46}$ \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 (\omega_c \approx 0.05$ eV), \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} (\omega_c \approx 0.1$ eV), as well as in the electron-doped material$^{47}$ \text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4+\delta (\omega_c \approx 0.06$ eV). In all of these cases the integral saturates and is constant to over 0.5 eV. In contrast, only about 80% of the spectral weight in underdoped \text{YBa}_2\text{Cu}_3\text{O}_{6.60} has formed by 800 cm$^{-1}$; the 90% threshold is not reached until $\approx 1800$ cm$^{-1}$ and the remaining spectral weight is recovered only at much higher frequencies ($\omega_c \gtrsim 5000$ cm$^{-1}$). In the case of the underdoped material, the plot has only been shown to the point where the FGT sum rule is recovered. If the plot is extended to $\sim 1$ eV, then the integral will increase to a value about $\approx 3\%$ over unity, which is within the estimated error for the FGT sum rule. This slow increase above unity may be an indication of one of two things: (i) $\omega_c$ may be larger than has been previously estimated, which would be consistent with estimates of $\omega_c \approx 2$ eV in the underdoped \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ materials,$^{22}$ or (ii) it is possible that when the sum rule is extended to high frequencies (i.e. of the order of eV) it may be incorporating temperature-dependent bound excitations. However, the absence of this behavior in the optimally-doped system suggests that such an excitation is restricted to the underdoped materials.

It is tempting to draw an analogy with the BCS dirty-limit case and argue that the spectral weight in the underdoped material has been pushed to higher frequency in response to an increase in the normal-state scattering rate. However, there are two important points that argue against this interpretation. First, an examination of scattering rate in the insets of Fig. 4 for $T \gtrsim T_c$ indicates that the $1/\tau_{sc} (\omega \rightarrow 0)$ $\lesssim 200$ cm$^{-1}$ for both materials. Second, if the conductivity is fitted using a two-component Drude-Lorentz model, then the nature of the low-frequency conductivity places hard constraints on the width of the Drude peak;$^{48}$ for $T \gtrsim T_c$ then $G \gtrsim 140$ cm$^{-1}$ for optimally-doped \text{YBa}_2\text{Cu}_3\text{O}_{6.95}$, and $G \approx 100$ cm$^{-1}$ for underdoped \text{YBa}_2\text{Cu}_3\text{O}_{6.60}. In each case, $G < 2 \Delta_0$, indicating that while $T$ may have an unusual temperature dependence, close to $T_c$ these materials are not in the dirty limit. Thus, the larger energy scale in the underdoped system has a different origin. While none of the cuprate superconductors are truly good metals, it has been suggested that for $T \gtrsim T_c$ the overdoped materials may resemble a Fermi liquid.$^{49}$ The rapid convergence of $\rho_{ac}$ in the optimally-doped material is what would be expected in a BCS system in which the normal state is a Fermi liquid. On the other hand, it is recognized that the underdoped materials are bad metals$^{50}$ and exhibit non-Fermi liquid behavior, and $\omega_c \gg 2\Delta_0$ is required to recover the FGT sum rule. The two types of behavior observed in the optimal and underdoped materials suggests that the nature of the electronic correlations in the normal state play a role in determining the different aspects of the superconductivity observed in these materials.$^{19}$

C. Kinetic energy and the sum rule

The unconventional nature of the superconductivity in the cuprate systems has lead to the suggestion that the condensation may be driven by changes in the kinetic rather than the potential energy.$^6$ In such a case the FGT sum rule for the in-plane conductivity must be modified to take on the form$^7$

$$\rho_s = \frac{120}{\pi} \int_{0+}^{\omega_c} \left[ \sigma_{1,n}(\omega) - \sigma_{1,s}(\omega) \right] d\omega$$

$$+ \frac{e^2 a^2}{\pi \epsilon^2 h^2} \left[ \langle -T_s \rangle - \langle -T_n \rangle \right],$$

where $a$ is the lattice spacing, and $T$ is that part of the in-plane kinetic energy associated with the valence band.$^{7,8}$ and the subscripts $n$ and $s$ refer to $T \simeq T_c$ and $T \ll T_c$, respectively. (The expression has a slightly different form for the $c$ axis.$^{51-53}$) The low-frequency term $\delta A_t$ is simply the FGT sum rule, while $\delta A_h$ corresponds to the high-frequency part of the integral, which is in fact the kinetic energy contribution. In a system where the kinetic energy plays a prominent role the FGT sum rule may appear to be violated. However, the maximum condensation energy for \text{YBa}_2\text{Cu}_3\text{O}_{6.95} based on specific heat measurements$^{54,55}$ is about 0.2 meV per (in-plane) copper atom. Assuming that the condensation energy is due entirely to the changes in the in-plane kinetic energy, this yields $\delta A_h \approx 2 \times 10^5$ cm$^{-2}$, which represents less than 0.3% of the spectral weight of the condensate.$^{56}$ Because of the limited accuracy of the FGT sum rule no statement may be made regarding changes in the in-plane kinetic energy. However, the general observation that the in-plane sum rule is preserved may have consequences for the $c$ axis.

D. Sum rules along the $c$ axis

The optical properties of \text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ have been examined in some detail along the poorly-conducting $c$ axis.$^{57-60}$ The optical conductivity (especially in the underdoped materials) is dominated by the unscreened phonons.$^{61,62}$ Given that large changes in the phonon
spectrum have been observed at low temperature in the underdoped materials, the application of the FGT sum rule must be treated with some care; in the studies cited here, the integral has been truncated at \( \omega_c \simeq 800 \text{ cm}^{-1} \) (0.1 eV). The application of the FGT sum rule along the \( c \) axis has shown that while this sum rule is not violated in the optimally-doped materials, as these materials become increasingly underdoped and a pseudogap has formed, the FGT sum rule is violated to varying degrees, with more than 50% of the \( c \)-axis spectral weight is missing at low temperature.\(^{16,17,66}\) The violation of the FGT sum rule has been proposed as evidence for a kinetic energy contribution,\(^{51,52}\) although there have also been other interpretations of this phenomena.\(^{53,67}\) The implication is that the missing spectral weight is recovered at high frequency, but it is unclear at precisely what point this occurs. In underdoped material, if the value for \( \omega_c = 800 \text{ cm}^{-1} \) in the optimally-doped materials is used, then the in-plane FGT sum rule will appear to be violated. However, it has been shown that extending the integral from \( \omega_c \simeq 800 \) to \( \gtrsim 5000 \text{ cm}^{-1} \) results in the recovery of the in-plane sum rule. We speculate that if the cut-off frequency for the FGT sum rule along the \( c \) axis is increased to the same value where the in-plane sum rule was recovered (\( \omega_c \gtrsim 5000 \text{ cm}^{-1} \)) then the spectral weight would be recovered and the \( c \) axis sum rule would yield \( \rho_{s,c} \). However, the general consensus at this time is that the conductivity data is not yet sufficiently precise along the \( c \) axis to confirm this prediction, so this remains a subject of some debate.

IV. CONCLUSIONS

In the BCS model the relevant energy scale to recover the strength of the condensate \( \rho_s \) is the superconducting energy gap (\( \omega_c \simeq 2\Delta \)), slightly larger in the dirty-limit case. Conductivity and FGT sum rules have been examined for light polarized along the \( a \) axis direction in the optimally doped \( \text{YBa}_2\text{Cu}_3\text{O}_6.95 \) and underdoped \( \text{YBa}_2\text{Cu}_3\text{O}_6.60 \) high-temperature superconductors to study the evolution of the spectral weight in these materials. Within the sensitivity of the experiment the FGT sum rule is obeyed in both materials. The energy scale required to recover the full strength of the condensate in the optimally doped material is \( \omega_c \simeq 800 \text{ cm}^{-1} \) (\( \simeq 2\Delta_0 \)), in good agreement with the predicted behavior of the BCS model. However, the energy scale in the underdoped materials is much higher, \( \omega_c \gtrsim 5000 \text{ cm}^{-1} \). This effect can not be attributed to dirty-limit effects in response to increased normal-state scattering, since for \( T \simeq T_c, \Gamma < 2\Delta_0 \) in both materials. The two types of behavior above and below \( T_c \) observed in the optimal and underdoped materials suggests that the nature of the electronic correlations in the normal state determine the different aspects superconductivity in these materials,\(^{19}\) and the degree to which the kinetic energy may play a role.

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\(^{1}\) D. Y. Smith, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, New York, 1985), pp. 35–68.

\(^{2}\) R. A. Ferrell and R. E. Glover, III, Phys. Rev. 109, 1398 (1958).

\(^{3}\) M. Tinkham and R. A. Ferrell, Phys. Rev. Lett. 2, 331 (1959).

\(^{4}\) J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

\(^{5}\) M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1966).

\(^{6}\) J. Hirsch, Physica C 199, 305 (1992).

\(^{7}\) J. E. Hirsch and F. Marsiglio, Phys. Rev. B 62, 15131 (2000).

\(^{8}\) J. E. Hirsch and F. Marsiglio, Physica C 331, 150 (2000).

\(^{9}\) M. R. Norman, M. Randeria, B. Jankó, and J. C. Campuzano, Phys. Rev. B 61, 14742 (2000).

\(^{10}\) R. Haslinger and A. V. Chubukov, Phys. Rev. B 67, 140504 (2003).

\(^{11}\) P. A. Lee, Physica C 317, 194 (1999).

\(^{12}\) P. W. Anderson, Physica C 341–348, 9 (2000).

\(^{13}\) V. J. Emery and S. A. Kivelson, J. Phys. Chem. Solids 61, 467 (2000).

\(^{14}\) V. E. Alexandrov and N. F. Mott, *High Temperature Superconductors and Other Superfluids* (Taylor and Francis, London, 1994).

\(^{15}\) M. V. Klein and G. Blumberg, Science 283, 42 (1999).

\(^{16}\) D. N. Basov, S. I. Woods, A. S. Katz, E. J. Singley, R. C. Dynes, M. Xu, D. G. Hinks, C. C. Homes, and M. Strongin, Science 283, 49 (1999).

\(^{17}\) D. N. Basov, C. C. Homes, E. J. Singley, M. Strongin, T. Timusk, G. Blumberg, and D. van der Marel, Phys. Rev. B 63, 134514 (2001).

\(^{18}\) T. Timusk and B. Statt, Rep. Prog. Phys. 62, 61 (1999).

\(^{19}\) M. R. Norman and C. Pépin, Phys. Rev. B 66, 100506 (2002).

\(^{20}\) D. van der Marel (private communication).

\(^{21}\) H. J. A. Molegraaf, C. Presura, D. van der Marel, and P. H. K. adn M. Li, Science 295, 2239 (2002).
