Interlayer Conductivity in the Superconductor $Tl_2Ba_2CuO_{6+\delta}$: Energetics and Energy Scales

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Abstract

We report on infrared studies of the $c$-axis electrodynamics of $Tl_2Ba_2CuO_{6+\delta}$ crystals. A sum rule analysis reveals spectral weight shifts that can be interpreted as a kinetic energy change at the superconducting transition. In optimally doped crystals, showing an incoherent normal state response, the kinetic energy is lowered at $T < T_c$, but no significant change is found in the over-doped samples, which have more coherent conductivity at $T > T_c$.

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Despite extensive experimental effort in high-$T_c$ superconductivity over the last decade very little is known about the microscopic roots of the condensation energy $E_c$ in this class of materials. In conventional superconducting metals $E_c$ is due to the reduction of the potential energy, which overwhelms the increase of the electronic kinetic energy [1]. Several models of high-$T_c$ superconductivity propose entirely different energetics of $E_c$ with the superconducting state being driven by changes of the Coulomb energy [4], exchange energy [5–9] or kinetic energy [10–12,3]. Existing experimental results are inconclusive [10–12,3].

A variety of models enable inference of the electronic kinetic energy from a sum rule analysis of the complex optical conductivity [3,4] or kinetic energy [5–9]. Typically, the $\sigma$-analysis of the complex optical conductivity [3,4] or kinetic energy [5–9] reveals a crossover to a more coherent response. In conventional superconducting metals $E_c$ is due to the reduction of the potential energy, which overwhelms the increase of the electronic kinetic energy [1]. Several models of high-$T_c$ superconductivity propose entirely different energetics of $E_c$ with the superconducting state being driven by changes of the Coulomb energy [4], exchange energy [5–9] or kinetic energy [10–12,3]. Existing experimental results are inconclusive [10–12,3].

For the case of a superconductor Eq. (1) can be rephrased in the form of a modified Ferrel-Glover-Tinkham (FGT) sum rule to yield the kinetic energy sum rule [6,8,14]:

$$\int_0^W d\omega \sigma_1(\omega) = -\alpha.$$  

(1)

In Eq. (2), $\rho_s$ is the superfluid density that quantifies the spectral weight under the superconducting $\delta$-function [15]. Integrals $N_n(\omega) = \int_0^\omega d\omega' \sigma_1(\omega', T > T_c)$ and $N_s(\omega) = \int_0^\omega d\omega' \sigma_1(\omega', T \ll T_c)$ are proportional to the number of carriers participating in absorption above and below $T_c$. The magnitude of $\rho_s = 4\pi\omega\sigma_2(\omega \to 0)$ and $[N_n - N_s]$ are obtained independently from the optical constants [12]. Typically, the $[N_n - N_s]$ integrals converge at energies below 10–15 $k_B T_c$ [16]. A comparison of the magnitudes of $\rho_s$ and $[N_n - N_s]$ then provides a basis for an experimental probe of the kinetic energy change $\Delta\alpha = [\alpha_n - \alpha_s]$. Physically, the non-vanishing magnitude of $\Delta\alpha$ implies that changes of the low-energy spectral weight in Eq. (1) are compensated by readjustment of interband transitions at $\omega > W$ so that the global sum rule $\int_0^\infty d\omega \sigma_1(\omega) = \frac{\pi e^2}{2m}$ is satisfied.

Recently, we found a $\rho_s > [N_n - N_s]$ inequality in the interlayer conductivity of a variety of cuprates indicating that the superconducting condensate is collected from an interband-scale energy range [17]. This result can be interpreted in terms of a reduction of the kinetic energy below $T_c$. In this paper we explore the connection between the development of coherence in the interlayer conductivity and the anomalous behavior of the c-axis superconducting condensate in $Tl_2Ba_2CuO_6+\delta$ (Tl-2201). We found that the energy scale associated with superconductivity extended to the interband region when the normal state conductivity across the layers was nearly blocked. Once the interlayer transport above $T_c$ became more coherent, the FGT sum rule approached exhaustion at energies below $\sim 5 k_B T_c$ suggesting that any kinetic energy change was very small or nonexistent.

$Tl_2Ba_2CuO_6+\delta$ is an ideal material for studying the over-doped regime of the phase diagram in which a variety of cuprates reveal a crossover to a more coherent response. Highly over-doped crystals of Tl-2201 have nearly identical chemical composition to the optimally doped phase since a less than 2% change in the oxygen content is required to suppress $T_c$ from the maximum value of $T_c \approx 90$ K down to less than 4 K [17]. Crystal preparation is described elsewhere [14]. Typical crystal dimensions were nominally 0.8 mm x 0.8 mm x 0.04 mm. Mosaics of several specimens with similar $T_c$ and $\Delta T_c$ (determined from magnetization measurements) were prepared and polished along a face parallel to the
c-axis. The polished surfaces were smooth, black, and shiny. Infrared reflectance, $R_c(\omega)$, was measured with $E \parallel c$ polarized light in the frequency range from 16 to 15,000 cm$^{-1}$. Spectra taken at different temperatures had a relative experimental uncertainty of less than 0.5%.

In Fig. 1, we show the raw reflectance results for the optimally and over-doped crystals. The $E \parallel c$ reflectance of both samples over the range of 80 to 2000 cm$^{-1}$ (10 to 250 meV) resembled an ionic insulator with a low reflectivity punctuated by phonon peaks. Both samples showed a plasma edge below $T_c$. Classical electrodynamics describes the development of this plasma edge since superconducting currents flow along all crystallographic directions [18]. In the optimally doped sample ($T_c = 81$ K, $\Delta T_c \approx 8$ to 10 K) the plasma edge grew out of an apparently insulating normal state spectrum. In the over-doped sample ($T_c = 32$ K, $\Delta T_c \approx 5$ K) we found a “metallic” up-turn in $R_c(\omega)$ measured above $T_c$, consistent with more coherent delocalized behavior. Below $T_c$, the reflectance continued to rise, and the plasma edge developed a characteristic minimum at a frequency position of $\omega = 49$ cm$^{-1}$. The minimum in reflectance was shifted to higher frequencies compared to $\omega = 37$ cm$^{-1}$ in the optimally doped case and was less sharply defined.

The raw $E \parallel c$ reflectance data was transformed using the Kramers-Kronig relations to determine the complex conductivity. Extrapolations of the reflectance data to low and high frequencies, required for the Kramers-Kronig integrals, did not strongly affect the results in the frequency range where measured data exists. The real part of the conductivity spectra were dominated by strong phonon peaks (Fig. 2). Three of the modes at 85, 151, 360 cm$^{-1}$ were unaffected by doping; the highest frequency mode softened from 602 cm$^{-1}$ in the optimally doped crystal down to 595 cm$^{-1}$ in the over-doped sample. The electronic background of the conductivity of the optimally doped sample was nearly flat and featureless for temperatures above and below $T_c$. The response of the over-doped crystal was different. The conductivity below 80 cm$^{-1}$ showed a Drude-like behavior steadily rising out of a $\sim 5$ (Ω cm)$^{-1}$ background. Below $T_c$, this “metallic” response diminished as temperature was lowered. By $T = 5$ K, it effectively vanished, and the conductivity (ignoring phonon peaks) was nearly frequency independent. Just above $T_c$, the dc conductivity of the over-doped sample at $T = 35$ K (obtained from the extrapolation of $\sigma_1(\omega)$ to $\omega = 0$) was $\sim 15$ (Ω cm)$^{-1}$. This is roughly a factor of 3 higher than the value obtained for optimally doped Tl-2201 crystals. It has been established that increasing oxygen content causes the c-axis to contract [19]. This closer spacing of the CuO$_2$ planes favors enhanced interlayer coupling and likely leads to the more coherent behavior of the conductivity. It is important to emphasize, however, that the c-axis conductivity is still two orders of magnitude smaller than the in-plane dc conductivity, and it is 4 to 6 orders of magnitude smaller than the conductivity of conventional metals.

Using the complex conductivity spectra above and below $T_c$, we can identify the spectral origins of the superfluid condensate. In all of our measurements, the conductivity at $T < T_c$ was suppressed compared to spectra taken at $T \approx T_c$, but we saw no evidence of a classical superconducting gap $\Delta$ for $T \ll T_c$. The absolute value of $\sigma_1(\omega)$ persisted well above the noise level down to the lowest measured frequencies, behavior consistent with gaplessness. To quantify the transfer of spectral weight below $T_c$, we plotted the ratio $[N_n(\omega)-N_s(\omega)]/\rho_s$ as a function of $\omega$ in Fig. 3 [12]. The superfluid density $\rho_s$ was determined from the extrapolation of $\omega \sigma_2(\omega,T)$ to $\omega = 0$ for $T \ll T_c$, a procedure that does not require model-dependent
assumptions [23]. The frequency dependence of \([N_n(\omega) - N_s(\omega)]/\rho_s\) unfolds the sum rule integrals. In the optimally doped sample, the ratio rose slowly and saturated near a value of about 0.6 at \(\omega \simeq 30 - 40\) meV. The energy interval in Fig. 3 corresponds to \(\sim 22\) \(k_B T_c\), more than sufficient for the conventional FGT sum rule. The data for the optimally doped sample implied that a significant portion of \(\rho_s\) was accumulated from energies above 0.15 eV. In contrast, in over-doped Tl-2201 the dominant fraction of the superfluid density was collected from the far-infrared, low energy region. Within our experimental uncertainty, at least 80 to 90\% of \(\rho_s\) was accumulated from energies as small as 4 - 5 \(k_B T_c\) [24]. Comparison of the data plotted in Fig. 2 and in Fig. 3 suggests that the behavior of the conductivity above \(T_c\) determines the energy scales from which the superconducting condensate is collected. In the case of the over-doped crystal there is no need to extend integration of the conductivity to mid-infrared and near-infrared energies in order to account for the magnitude of \(\rho_s\) since the required spectral weight is readily available at low energies.

If Eq. (2) is chosen as the basis for data interpretation, then the \(\rho_s > [N_n - N_s]\) inequality observed in the optimally doped crystal implies a reduction of the electronic kinetic energy below \(T_c\). The reduction of the kinetic energy can be understood by noting that the charge carriers are nearly confined to the CuO2 planes above \(T_c\) whereas in the superconducting state \(paired\) charges move more easily between the layers. On the contrary, the over-doped sample, which revealed a more coherent \(c\)-axis response (Drude-like upturn of \(\sigma_1(\omega)\) and enhanced \(dc\) conductivity), showed \(\Delta \alpha \simeq 0\) within our error bars. The data suggested that a kinetic energy change is observed only if deconfinement of the charge carriers occurs by virtue of pair tunneling below \(T_c\). If the charge carriers were already delocalized in the normal state (even with very low plasma frequencies), then the magnitude of \(\Delta \alpha\) is vanishingly small. The same trend was observed in the \(c\)-axis response of the \(YBa_2Cu_3O_x\) (YBCO) family. The discrepancy between \([N_n(\omega) - N_s(\omega)]\) and \(\rho_s\), suggesting a lowering of the kinetic energy, was most extreme in \(YBa_2Cu_3O_{6.53}\). As the oxygen content was raised, the excess spectral weight appeared in the lower energy part of \(\sigma_1(\omega, T > T_c)\) spectra. The \([N_n(\omega) - N_s(\omega)]/\rho_s\) ratio with integration limited up to 10-15 \(k_B T_c\) was near unity for \(YBa_2Cu_3O_{6.85}\) and higher doping levels indicating that \(\Delta \alpha\) became vanishingly small [22].

Further analysis of the over-doped Tl-2201 crystal showed a lower energy scale associated with superconductivity. It has been experimentally observed in a wide variety of cuprates that the magnitude of the \(c\)-axis penetration depth \(\lambda_c = c/\sqrt{\rho_s}\) is related to the \(dc\) conductivity \(\sigma_{dc}\) at \(T \simeq T_c\) by the relationship

\[
\lambda_c^{-2} = \frac{1}{\hbar c^2} \Omega_s \sigma_{dc}(T \simeq T_c),
\]

where \(\Omega_s\) is an energy scale associated with superconductivity [23 25 26]. Eq. (3) may be obtained either by modeling a dirty limit bulk superconductor or by treating the anisotropic cuprates as a weakly coupled stack of intrinsic Josephson junctions. Those models find \(\Omega_s = 4\pi^2 \Delta\). In our experiments, \(\lambda_c\) remained nearly unchanged [20] whereas the \(c\)-axis \(dc\) conductivity increased by a factor of \(\sim 3\) in the over-doped crystals. If Eq. (3) holds true, then \(\Omega_s\) must be reduced in the over-doped regime in order to keep the penetration depth constant. Supporting evidence that \(\Omega_s\) is indeed reduced for over-doped Tl-2201 comes from Raman scattering measurements on optimally and over-doped Tl-2201 which found that a spectral feature attributed to the superconducting energy gap \(2\Delta\) shifted down in frequency from \(\sim 350\) cm\(^{-1}\) in optimally doped Tl-2201 to \(\sim 105\) cm\(^{-1}\) in an over-doped sample as
$T_c$ fell from 78 K to 37 K [26,27]. $c$-Axis polarized Raman scattering in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) single crystals also showed an energy scale that diminished in over-doped samples [28]. The lower energy scale of the superfluid condensation seen in Fig. 3 is consistent with a reduction in $\Omega_S$ [29].

Several important distinctions of over-doped phases from the optimally-doped counterparts have been observed in different families of the cuprates. Raman spectroscopy showed both in Tl-2201 and Bi-2212 single crystals highly anisotropic energy gaps at optimal doping but revealed a crossover to isotropic behavior in over-doped samples [24]. Consistent with this latter result, angular resolved photoemission (ARPES) on Bi-2212 found that the Fermi surface nodes vanished in the over-doped regime [31]. Thus, both Raman and ARPES studies suggested a trend towards the development of a more isotropic superconducting state in over-doped crystals. We observed a more conventional superfluid response in over-doped Tl-2201 compared to the optimally-doped sample. Phase sensitive measurements of the order parameter in over-doped materials are needed to determine if the above observations are associated with the development of an $s$-component of the order parameter. An $s$-wave component in the order parameter in the over-doped regime is possible within the stripe-based models [4].

Based on the existing experimental results we were unable to correlate changes in the kinetic energy with the critical temperature of the studied superconductors. In the Tl-2201 series, $\Delta\alpha$ is largest in the optimally-doped crystals. The YBCO data, however, revealed large changes of $\alpha$ in the underdoped regime whereas in the optimally doped samples the effect was negligible [12]. The common parameter determining the kinetic energy change for both series of crystals appears to be the dc conductivity. It remains to be seen if the absolute value of $\Delta\alpha$ is sufficient to account for the condensation energy determined from specific heat measurements [10,11,8].

In conclusion, we employed infrared spectroscopy to examine the energy scales of superconducting state in Tl-2201. We found that the superfluid spectral weight was accumulated from lower energies when the $c$-axis conductivity showed a more coherent, delocalized response. Using the modified FGT sum rule we could extract kinetic energy changes and correlate this change to the normal state $c$-axis conductivity.

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[21] The peaks at approximately 45 and 75 meV in the over-doped sample data in Fig. 3 are due to the slight temperature dependence of unsubtracted $c$-axis phonons. The phonons have been removed in the optimally doped data since they showed a much stronger temperature dependence. Data with phonons can be found in [22].

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FIGURES

FIG. 1. Reflectance of Tl-2201 measured with $E \parallel c$ polarization of incident radiation. Left panel: The optimally doped sample develops a superconducting plasma edge out of an apparently insulating spectrum for $T < T_c$. Right panel: At the lowest energies, the over-doped sample shows continuously increasing reflectance above and below $T_c$.

FIG. 2. Real part of the complex conductivity of Tl-2201 calculated from the reflectivity shown in Fig. 1. Left panel: The conductivity of the optimally doped sample is punctuated by phonon peaks but is otherwise nearly flat and featureless. Right panel: The over-doped sample shows the same phonon peaks but develops a coherent, Drude-like peak for $T > T_c$ that condenses into the superfluid condensate when $T < T_c$.

FIG. 3. The ratio of the spectral weight difference $[N_N(\omega) - N_S(\omega)]$ to the superfluid density $\rho_s$ as described in the text for optimally ($T_c = 81$ K) and over-doped ($T_c = 32$ K) Tl-2201. The superfluid condensate is accumulated from lower energies in the over-doped sample. To calculate the over-doped curve, we extrapolated (shown as a dashed line) $\sigma_1(\omega, T = 35$ K) from $\omega = 16$ cm$^{-1}$ to $\omega = 0$ using a Drude function with $\sigma_{dc} = 15$ (Ω cm)$^{-1}$ and $\tau^{-1} = 45$ s$^{-1}$ and $\sigma_1(\omega, T = 5$K) = 5 (Ω cm)$^{-1}$.
Fig. 1
A.S. Katz et al.
Interlayer Conductivity in the Superconductor Tl-2201
$T_c = 81$ K

$T_c = 32$ K
(over-doped)

$\sigma(\omega) \left( \Omega \text{ cm} \right)^{-1}$

$\omega$ (meV)

meV

meV

wavenumber (cm$^{-1}$)

wavenumber (cm$^{-1}$)

$T_c = 81$ K

$T_c = 32$ K

$35$ K

$80$ K

$17$ K

$5$ K

$90$ K

$15$ K

$0$  $5$  $10$  $15$  $20$  $25$

$0$  $5$  $10$  $15$  $20$  $25$

Fig. 2
A.S. Katz et al.
Interlayer Conductivity in the Superconductor Tl-2201
$T_c = 32 \text{ K, } \omega_{ps} = 134 \text{ cm}^{-1}$

$T_c = 81 \text{ K, } \omega_{ps} = 130 \text{ cm}^{-1}$