Heat Transport in a Strongly Overdoped Cuprate: Fermi Liquid and a Pure *d*-Wave BCS Superconductor

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The transport of heat and charge in the overdoped cuprate superconductor $Tl_2Ba_2CuO_{6+\delta}$ was measured down to low temperature. In the normal state, obtained by applying a magnetic field greater than the upper critical field, the Wiedemann-Franz law is verified to hold perfectly. In the superconducting state, a large residual linear term is observed in the thermal conductivity, in quantitative agreement with BCS theory for a *d*-wave superconductor. This is compelling evidence that the electrons in overdoped cuprates form a Fermi liquid, with no indication of spin-charge separation.

A fundamental question about the rich and baffling behavior of electrons in high-temperature superconductors is whether or not it can be understood in the framework of Fermi-liquid (FL) theory, the standard theory of electrons in solids. Several authors believe that when the concentration of electronic carriers in these cuprate materials is sufficiently low, as in the so-called underdoped region of the doping phase diagram, the basic excitations of the electron system are not the usual Landau quasiparticles characteristic of FL theory. In one class of proposals [1–3], for example, the electron is thought to fractionalize into a neutral spin-carrying excitation, called a "spinon," and a spinless charge-carrying excitation, called a "holon" or "chargon." However, to this day, such "spin-charge separation" has not been confirmed experimentally. On the other hand, after 15 years of intensive research it is still not known with any certainty whether or not the ground state of cuprates is a Fermi liquid in any region of the phase diagram. It is widely assumed that in the metallic-like overdoped regime at high carrier concentration FL theory does hold, but there is little solid evidence to support this lore.

In this Letter, we present the results of a study which show that strongly overdoped cuprates do not undergo spin-charge separation and their ground state is most likely a Fermi liquid. By measuring the transport of both heat and charge in the normal state at very low temperature, we were able to verify that one hole-doped cuprate in the overdoped regime obeys the Wiedemann-Franz (WF) law. This universal law is a robust signature of FL theory, stating simply that the electronic carriers of heat are fermionic excitations of charge *e*. In addition, the thermal conductivity in the superconducting state is found to be in good agreement with BCS theory for a superconductor with a pure *d*-wave order parameter.

The particular compound chosen for this study is $Tl_2Ba_2CuO_{6+\delta}$, because it can easily be overdoped. In many ways, it is the ideal cuprate material. Its crystal structure is tetragonal, without the CuO chains that com-

plicate the properties of the orthorhombic compounds $YBa_2Cu_3O_{7-\delta}$ (Y-123) and $YBa_2Cu_4O_8$, or the buckling that alters the unit cell of $Bi_2Sr_2CaCu_2O_8$ (Bi-2212). It is made of a stack of single CuO_2 planes and is therefore not subject to possible bilayer effects such as encountered in Bi-2212. It has a high maximum critical temperature T_c^{max} of 90 K, at optimal doping, much as in Y-123 and Bi-2212. In this sense, it is free of the possible concerns about the low T_c found in single-plane $La_{2-x}Sr_xCuO_4$ (LSCO). Finally, the $d_{x^2-y^2}$ symmetry of its superconducting state has been confirmed by phase-sensitive measurements, at least at optimal doping [4].

Mackenzie *et al.* measured the resistivity of a strongly overdoped crystal of Tl-2201, with $T_c = 15$ K [5]. In zero magnetic field, $\rho(T)$ was found to follow roughly a power law of $T^{1.8}$ from room temperature down to T_c and extrapolate to $\rho_0 \simeq 7$ $\mu\Omega$ cm at $T = 0$. The resistive upper critical field at $T \to 0$, $H_{c2}(0)$, is between 12 and 16 T (for fields perpendicular to the conducting CuO_2 planes, i.e., $H \parallel c$), depending on the precise criterion.

The overdoped samples of Tl-2201 used in this study were rectangular single crystals with typical dimensions of 0.4 and 0.2 mm in the tetragonal basal plane and 10 μm along the *c* axis. The voltage pads had a width of 25 μm and the spacing between the electrodes was 0.3 mm. They were grown by the same technique as used by Mackenzie and co-workers in previous studies [5–7]. They have $T_c \simeq 15$ K, in zero magnetic field. Using the empirical formula $T_c/T_c^{max} = 1 - 82.6(p - 0.16)^2$, this translates into a carrier concentration of $p = 0.26$ hole/Cu atom. To obtain such critical temperatures, the samples were annealed in 1 bar of flowing O_2 at 350 °C for 2 days. The resistivity of our samples is essentially identical to that obtained previously [5], with $\rho_0 = 5.6$ $\mu\Omega$ cm. Both heat and charge transport were measured using the same contacts, made by diffusing silver epoxy. A typical value for the contact resistance was 0.1 Ω at 4 K. The thermal conductivity was measured down to below 100 mK with a standard one-heater

two-thermometer technique in a dilution refrigerator. The magnetic field was applied along the c axis. The geometric factor used to convert from resistance (electrical or thermal) to electrical resistivity ρ or thermal conductivity κ was set by requiring that $\rho(300 \text{ K}) = 180 \ \mu\Omega \text{ cm}$, the value obtained in previous studies of numerous crystals with the same doping level [5–8]. The uncertainty on this value is estimated at $\pm 10 \ \mu\Omega$ cm.

The resistivity is shown in Fig. 1, for fields ranging from zero to above $H_{c2}(0)$. A slight positive magnetoresistance is observed, in agreement with previous work [7]. The resistivity below 30 K (and above T_c) is best fit by the function $\rho = \rho_0 + bT + cT^2$, with a substantial linear term (i.e., $bT > cT^2$ for $T < 15$ K). The fitting parameters are $\rho_0(H) = 5.84$, 5.99, and 6.15 $\mu\Omega$ cm at $H = 7$, 10, and 13 T, respectively, and $b = 0.064 \ \mu\Omega \text{ cm K}^{-1}$, $c = 0.0054 \ \mu\Omega \text{ cm K}^{-2}$ at 13 T. This unusual dependence was reported previously [8] and interpreted as "non-Fermi-liquid" behavior, in the sense that no linear term is expected in conventional FL theory. Deviations from the standard T^2 dependence have been observed in a number of heavy-fermion materials, for example, $T^{1.2}$ in $CePd_2Si_2$ below 20 K [9]. In these materials, this is associated with the proximity to a quantum critical point (QCP), where antiferromagnetic order sets in as a function of pressure or chemical composition. In the case of cuprates, the obvious QCP would be the onset of superconductivity at a critical concentration p_c close to 0.3 hole/Cu atom, but a QCP has also been postulated to exist inside the superconducting region.

The thermal conductivity κ is shown in Fig. 2. The data are plotted as κ/T vs T^2 to separate the contribution of electrons from that of phonons, given that the asymptotic dependence of the former as $T \rightarrow 0$ is linear in T while that of the latter is cubic. In other words, in Fig. 2, the electronic contribution is the residual linear term κ_0/T given by the intercept of a linear fit with the $T = 0$ axis. The value of κ_0/T obtained in this way is 1.41, 2.76, 3.47, 3.75, 3.87, 3.90, 3.95, and 3.95 mW K^{-2} cm^{-1}, at $H =$ 0, 1, 2.5, 4, 5.5, 7, 10, and 13 T, respectively. As explained above, the uncertainty on the overall absolute value is approximately $\pm 5\%$. However, the relative uncertainty, e.g., between different fields, is much lower, around 1%. This high degree of reliability is due to the fact that in these samples electrons conduct much better than phonons, and hence the slope of $\kappa(T)/T$ in Fig. 2 is weak relative to the intercept. Note that at high fields, electrons scatter phonons very effectively and $\kappa(T)$ is entirely electronic below 1 K.

Fundamentally, the linear term in κ at $T = 0$ reveals the presence of fermionic excitations in the electron system. We can then ask whether these excitations carry charge. This question can be addressed only in the absence of any superfluid that can also carry charge, which amounts to testing the WF law in the normal state. This law is one of the most fundamental properties of a Fermi liquid, reflecting the fact that the ability of a quasiparticle to transport energy is the same as its ability to transport charge, provided it cannot lose energy through collisions. It states that the heat conductivity κ and the electrical
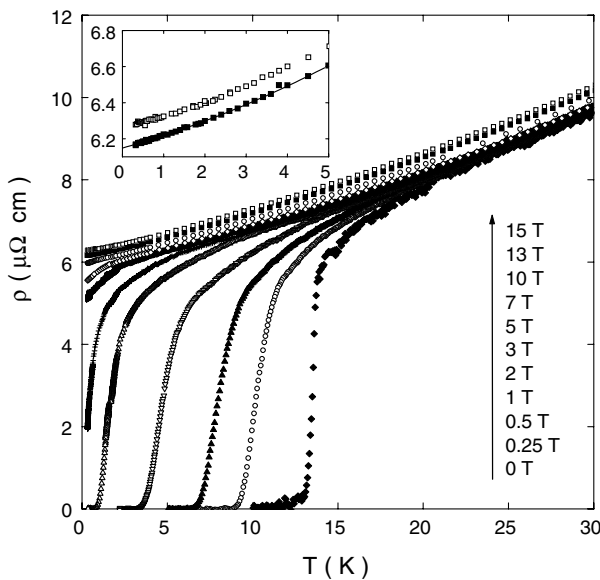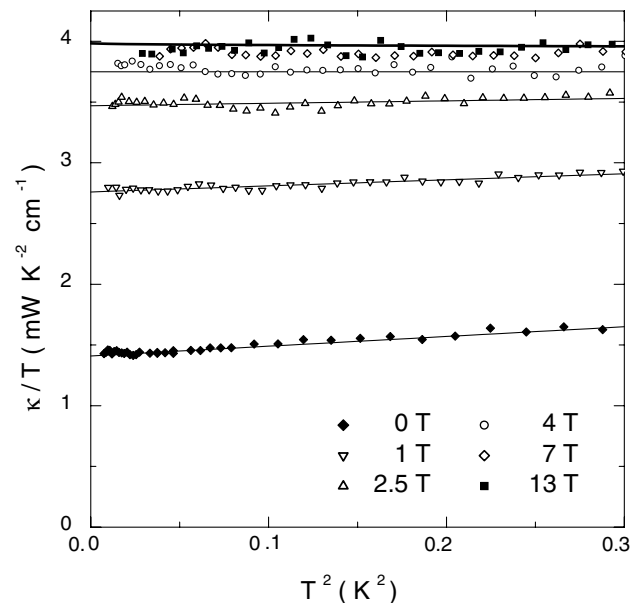

FIG. 1.   Electrical resistivity of Tl-2201 vs temperature for a current in the basal plane at different values of the magnetic field applied normal to the plane. All trace of superconductivity has vanished by 13 T. Inset: $\rho(T)$ at $H = 13$ T (filled symbols) and 15 T (open symbols). The line is a fit of the 13 T data to the functional form $\rho(T) = \rho_0 + bT + cT^2$.

FIG. 2.   Thermal conductivity of Tl-2201 for a heat current in the basal plane, plotted as κ/T vs T^2, at different values of the magnetic field applied normal to the plane. The thin lines are linear fits to the data. The thick line is $L_0/\rho(T)$ where $\rho(T)$ is a fit to the resistivity at 13 T (see inset of Fig. 1).

conductivity σ of a metal are related by a universal constant:

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 \equiv L_0, \tag{1}$$

where T is the absolute temperature, k_B is Boltzmann's constant, and $L_0 = 2.44 \times 10^{-8}$ W Ω K^{-2} is Sommerfeld's value for the Lorenz ratio $L \equiv \kappa/\sigma T$. Theoretically, electrons are predicted to obey the WF law at $T \to 0$ in a wide range of environments: in both three and two dimensions (but not strictly in one dimension), for any strength of disorder and interaction [10], scattering, and magnetic field [11]. Experimentally, the WF law does appear to be universal at $T \to 0$: until recently, no material had been reported to violate it. The first exception was found in optimally doped Pr$_{2-x}$Ce$_x$CuO$_4$ (PCCO), an electron-doped cuprate [12].

It is in general difficult to test the WF law in cuprate superconductors because of their high upper critical fields. In our crystals, the superconductivity has completely vanished by 13 T, at which field we find $\kappa_0/T = 3.95 \pm 0.04$ mW K^{-2} cm^{-1} and $\rho_0 = 6.15 \pm 0.03$ $\mu\Omega$ cm, so that $L = \rho_0\kappa_0/T = 0.99 \pm 0.01 L_0$, in perfect agreement with the WF law. Note that the Lorenz ratio does not suffer from the 5% uncertainty associated with the geometric factor, as both transport measurements are performed using the same sample with the same contacts. The error bars are therefore on the order of 1%. In Fig. 2, the transport of heat and charge are compared directly by reproducing the charge conductivity at 13 T from Fig. 1. This is done by plotting $L_0/\rho(T)$ vs T using the fit to the 13 T data for $\rho(T)$ (inset of Fig. 1). The charge conductivity $L_0\sigma(T)$ is seen to be equal to the heat conductivity $\kappa(T)/T$ at 13 T.

The basic implication of this result is that *the fermions which carry heat also carry charge e and are therefore indistinguishable from standard Landau quasiparticles.* In particular, there is no evidence of any spin-charge separation. Indeed, if electrons were to fractionalize into neutral spin-carrying fermions (spinons) and charged bosons (chargons) [3], there would be no reason to expect the WF law to hold, as the heat-carrying fermions would not take part in the transport of charge. This result therefore imposes a constraint on theories of spin-charge separation (SCS): the critical hole concentration p_{SCS} at which electron fractionalization starts to occur is not the QCP where superconductivity starts to occur (on the overdoped side of the phase diagram), but can only be lower. In other words, any hypothetical onset of SCS must obey $p_{SCS} < 0.26 < p_c$. *It therefore appears that the mechanism for superconductivity in this overdoped region of the phase diagram is not the condensation of charge-e bosons,* but most likely Cooper pairing. Note that (barring any profound electron-hole asymmetry) this conventional picture is expected to break down

with underdoping, as suggested by the violation of the WF law in PCCO near optimal doping [12].

Although the standard FL description fails, as revealed by the nonquadratic T dependence of $\rho(T)$, the basic nature of the electronic excitations in the limit of zero energy is that of Landau FL quasiparticles. (A similar situation is seen in heavy-fermion materials [13].)

In the absence of a magnetic field, there is a large residual linear term in the thermal conductivity of Tl-2201, namely, $\kappa_0/T = 1.41$ mW K^{-2} cm^{-1}. A similar term has also been observed in other hole-doped cuprates, albeit at optimal doping, where it is much smaller: $\kappa_0/T = 0.14$, 0.15, and 0.11 mW K^{-2} cm^{-1}, in Y-123 [14], Bi-2212 [15,16], and LSCO [17], respectively. Within BCS theory applied to a d-wave superconductor, this residual heat conduction is expected, arising from zero-energy quasiparticles induced by impurity scattering near the nodes in the $d_{x^2-y^2}$ gap function. In the clean limit, where the scattering rate $\Gamma \ll k_B T_c/\hbar$, it is universal (in the sense that it is independent of Γ), and it depends only on the ratio of the two quasiparticle velocities (v_F and v_2) which govern the Dirac-like spectrum of nodal quasiparticles, $E = \hbar\sqrt{v_F^2 k_1^2 + v_2^2 k_2^2}$ [18]:

$$\frac{\kappa_0}{T} = \frac{k_B^2}{3\hbar}\frac{n}{c}\left(\frac{v_F}{v_2} + \frac{v_2}{v_F}\right), \tag{2}$$

where n is the number of CuO$_2$ planes per unit cell of height c (along the c axis), and $\vec{k}_1$ and $\vec{k}_2$ are unit vectors pointing in directions normal and tangential to the Fermi surface at the node, respectively. In other words, v_F is the Fermi velocity in the nodal direction and v_2 is proportional to the slope of the gap at the node, $d\Delta/d\phi = \hbar k_F v_2$, with k_F the Fermi wave vector.

Applying Eq. (2) to Tl-2201, for which $n = 2$ and $c = 23.2$ Å, we get $v_F/v_2 = 270$. A rough estimate using Fermi surface parameters typical of cuprates, namely, $v_F = 2.5 \times 10^7$ cm/s and $k_F = 0.7$ Å^{-1} (the values measured in Bi-2212 [19]), and the simplest d-wave gap function, $\Delta = \Delta_0 \cos 2\phi$, with the weak-coupling relation for a d-wave superconductor, $\Delta_0 = 2.14 k_B T_c$, gives $v_F/v_2 = 210$. This shows that the magnitude of κ_0/T is in good agreement with the simplest BCS analysis.

It should be recognized that even though the mean free path in these samples is rather long (in the range 500–1000 Å [8]), the scattering rate Γ is not small compared to T_c. It may be estimated using the standard expression for the normal state conductivity: $\kappa_N/T = \frac{1}{3}\gamma_N v_F^2 \tau$, where γ_N is the specific heat coefficient and $\tau = 1/(2\Gamma)$. With $\gamma_N \simeq 3$ mJ K^{-2} mole^{-1} [6] and $v_F = 2.5 \times 10^7$ cm/s, one gets $\hbar\Gamma \simeq 0.4 k_B T_c$. At finite Γ, corrections to Eq. (2) give an increase in κ_0/T [20]. Assuming $\Delta_0 = 2.14 k_B T_c$, the correction for $\hbar\Gamma/k_B T_c = 0.4$ is by a factor of approximately 1.5 [20]. Thus the correct value of v_F/v_2 is probably closer to $270/1.5 = 180$ [21].

It will be interesting to investigate the doping dependence of κ_0/T as a way of measuring the dependence of the gap function on carrier concentration, via v_2. In the absence of further data on Tl-2201, we may compare with optimally doped Y-123 ($T_c = 93$ K) or Bi-2212 ($T_c \simeq 90$ K), for which $v_F/v_2 = 14$ and 19, respectively [15]. (The value of 19 for Bi-2212 agrees very well with the value of 20 obtained from angle-resolved photoemission spectroscopy measurements of v_F and v_2 separately [15,19].) Under the assumption of a doping independent v_F, verified in both Bi-2212 [19] and LSCO [22], one immediately sees that v_2, or the magnitude of the gap (near the nodes), scales roughly with T_c. This strongly suggests that the standard BCS relation between gap magnitude and transition temperature, $\Delta_0 \propto T_c$, holds in the overdoped regime. This is in striking contrast with what is found in the underdoped region of the phase diagram. Indeed, our measurements on underdoped Y-123 and LSCO [23] reveal that v_F/v_2 *decreases* as T_c is reduced by underdoping (see also [24]).

Several authors have proposed the existence of a QPC within the superconducting dome in the phase diagram of cuprates, either as a theoretical prediction to explain the diagram itself or as suggested in various experiments. Its location is usually taken to be near optimal doping, in the neighborhood of $p = 0.2$. If it is associated with a change in the symmetry of the superconducting order parameter, Vojta *et al.* have argued that the most likely scenario is a transition from a pure $d_{x^2-y^2}$ state to a complex order parameter of the form $d_{x^2-y^2} + ix$, where x can have either s or d_{xy} symmetry [25]. Dagan and Deutscher have recently reported a split zero-bias anomaly in their tunneling on Y-123 thin films as soon as the material is doped beyond optimal doping, a feature which they attribute to the appearance of a complex component to the order parameter in the bulk [26]. The presence of a subdominant component ix in the order parameter causes the nodes to be removed, as the gap can no longer go to zero in any direction. The observation of a residual linear term in the thermal conductivity, a direct consequence of nodes in the gap, therefore excludes the possibility of any such subdominant order parameter. (More precisely, since our measurement goes down to 100 mK, it puts an upper bound on the magnitude of $|x|$ relative to $|d_{x^2-y^2}|$ at about 0.5%.) Moreover, there is no subdominant order parameter in Tl-2201 at optimal doping [4]. In other words, *if there truly is a QCP between optimal doping at $p \simeq 0.16$ and the critical point $p_c \simeq 0.3$, it does not appear to be associated with the onset of a complex component in the order parameter.*

In summary, the low-temperature transport properties of Tl-2201 with $T_c = 15$ K show that spin-charge separa-ration does not occur in strongly overdoped cuprates. The normal state at $T \to 0$ satisfies the Wiedemann-Franz law perfectly, demonstrating that the only electronic excitations carrying heat and charge are Landau quasiparticles. The superconducting state obeys BCS theory in that the residual heat conduction is of the expected magnitude for a d-wave gap and the dependence of the low-energy spectrum on doping strongly suggests that the gap scales with T_c in the conventional way. Finally, the possibility of a subdominant order parameter (*ix*) is ruled out.

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