Test of the Wiedemann-Franz Law in an Optimally Doped Cuprate

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We present a study of heat and charge transport in $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ focused on the size of the low-temperature linear term of the thermal conductivity at optimal-doping level. In the superconducting state, the magnitude of this term implies a d-wave gap with an amplitude close to what has been reported. In the normal state, recovered by the application of a magnetic field, measurement of this term and residual resistivity yields a Lorenz number $L = \kappa_N \rho_0 / T = 1.3 \pm 0.2 L_0$. The departure from the value expected by the Wiedemann-Franz law is thus slightly larger than our estimated experimental resolution.

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In spite of many years of intense research by a sizable fraction of the condensed-matter physics community, high T_c superconductivity remains a mystery. A central question is the extent of the validity of Landau's Fermi liquid picture to describe the elementary excitations of the ground state. High-T_c cuprates are doped Mott insulators and are host to a particularly strong Coulomb repulsion neglected in the Fermi liquid picture. It remains to be established, however, to what extent this becomes an obstacle for the formation of Landau quasiparticles in the $T = 0$ limit. A recent attempt to answer this question has been made by measuring the subkelvin thermal conductivity of the normal state in order to check for the validity of the Wiedemann-Franz law which is a robust signature of a Fermi liquid [1–3]. The validity of this universal law relating the magnitude of thermal and electrical conductivities is expected in the $T = 0$ limit, disregarding the fine details of electronic scattering and the Fermi surface. On the other hand, various scenarios based on electron fractionalization lead to its violation.

In this Letter, we present a first experimental study to check the validity of the Wiedemann-Franz (WF) law in a hole-doped cuprate at optimal-doping concentration. Recovering the normal state of $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ (Bi-2201) by the application of a strong magnetic field, we found a thermal conductivity slightly larger than what is expected by the WF law. The departure appears to be genuine as it is significantly larger than the experimental precision obtained in the verification of the WF law in a simple metal.

In-plane thermal conductivity (κ) in the presence of a magnetic field applied along the c axis was measured with a standard two-thermometers–one-heater setup which allowed one to measure the in-plane electric resistivity in the same conditions. Bi-2201 single crystals, with typical dimensions of $(2–8) \times (400–800) \times (600–900)\ \mu m^3$, were grown in a gaseous phase in closed cavities of a KCl solution melt as detailed elsewhere [4]. The doping level in stoichiometric $Bi_2Sr_2CuO_{6+\delta}$ can be modified by replacing Sr^{2+} either with Bi^{3+} or with La^{3+} [5,6]. We succeeded to make single-phase high quality crystals of $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ in the range of $0.17 < x < 0.7$. The maximum [resistive] T_c found in this system was $\sim$10.5 K in agreement with previous studies [4,6]. In $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$, on the other hand, the maximum T_c is 38 K [7]. Thus, the disorder associated with (Sr,Bi) substitution is apparently stronger than the one due to (Sr,La) doping and leads to a lower T_c and a higher residual resistivity in $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ compared to $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ [8].

An unambiguous determination of carrier concentration, p, in high-T_c cuprates other than $La_{2-x}Sr_xCu_2O_4$ (La-214) is not straightforward. However, by comparing Hall coefficients of various families of cuprates, Ando *et al.* [9] have shown that the magnitude of the renormalized Hall coefficient ($R_H e/V_0$, where V_0 is the volume associated with each Cu atom) is an appropriate measure of carrier concentration. In order to check the doping level of our samples, we measured the Hall coefficient in a number of them and found that the magnitude of $R_H e/V_0$ is close to what is expected for an optimal-doping cuprate. As seen in Fig. 1 which presents a typical curve, the magnitude of renormalized Hall coefficient is somewhere between the values obtained for La-214 at $p = 0.15$ and $p = 0.18$. A similar result has been recently reported by Ono and Ando [8]. Together with the linear resistivity observed from room temperature down to T_c (see the inset of Fig. 1), this provides compelling evidence that the physics of cuprates at the optimal-doping level can be explored in Bi-2201, which, contrary to other hole-doped cuprates, presents a resistive upper critical field within the range of available dc magnetic fields [4].

As the required field ($\sim$25 T), however, still exceeds the range provided by available commercial magnets, the

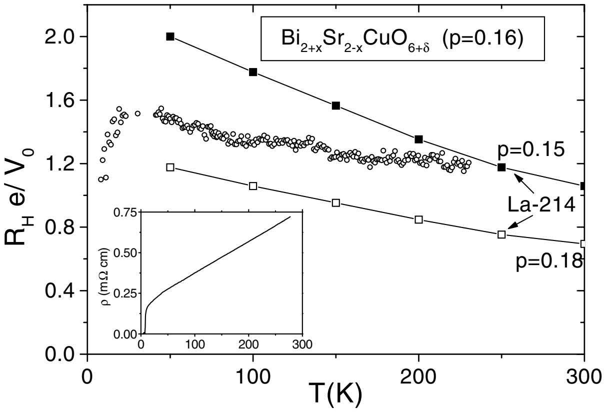

FIG. 1. Renormalized Hall coefficient in a $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ sample compared with the values reported for La-214 [10] for two different doping levels. The inset shows the temperature dependence of resistivity.

experiment was performed in a resistive magnet at the Grenoble High Magnetic Field Laboratory. Measuring subkelvin thermal conductivity in this context, we were faced with two major technical challenges. The first was to cool down the sample and thermometers held in vacuum to low temperatures in spite of strong mechanical vibrations associated with the circulation of cooling water. This problem was partially solved by designing a new insert with a vacuum chamber containing the entire thermal conductivity setup which was placed inside the mixing chamber of a Kelvinox top-loading dilution fridge [11]. The second was to measure accurately the temperature at high magnetic fields given the non-negligible magnetoresistance of the RuO_2 thermometers used in the setup and the absence of any zero-field zone. This second problem was resolved by using Coulomb blockade thermometry [12]. An array of 100 tunnel junctions provided by Nanoway (Finland) was attached to the cold finger and used as a field-independent thermometer [13] for calibrating the shift in the resistance of RuO_2 thermometers with the application of magnetic field.

Zero magnetic field.—Figure 2(a) displays the temperature dependence of thermal conductivity for three crystals of Bi-2201 at zero magnetic field. Since the lattice thermal conductivity is expected to display a cubic temperature dependence at very low temperatures, (κ/T) is plotted as a function of T^2 in order to extract a linear term, κ_0/T, associated with the electronic contribution. The magnitude of this linear term varies from 0.19 in the most underdoped sample ($p = 0.14$) to 0.40 mW/K^2 cm in the most overdoped sample ($p = 0.19$) [see Fig. 2(c)]. The doping level in these samples was estimated using the reported empirical relationship between T_c and carrier concentration in Bi-2201 [9]. Figure 2(b) presents the temperature dependence of resistivity in the same samples.

A finite κ_0/T is a consequence of heat transport by nodal quasiparticles of the d-wave superconducting gap.

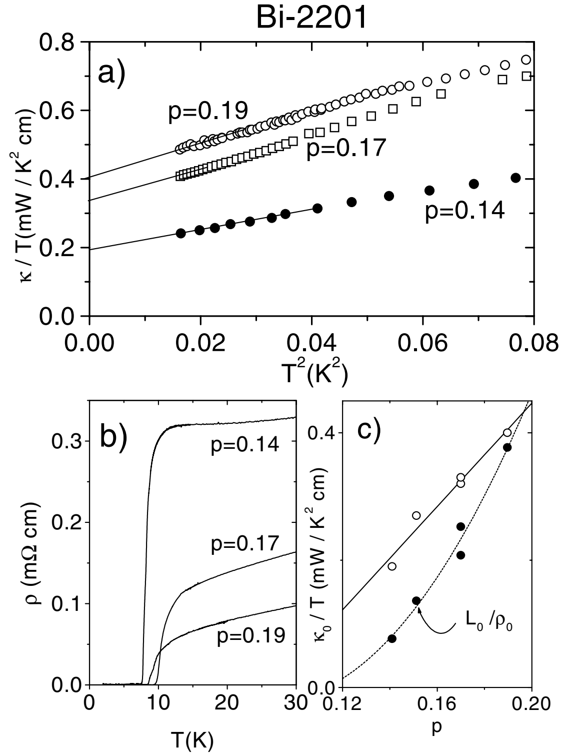

FIG. 2. (a) Subkelvin thermal conductivity in three different Bi-2201 single crystals. (b) Temperature dependence of the zero-field resistivity in the three samples. (c) A comparison between the doping dependence of κ_0/T (open circles) and of L_0/ρ_0 (solid circles). Lines are to guide the eye.

It has been already reported in a variety of hole-doped cuprates [14–18]. According to the theory of transport in a d-wave Bardeen-Cooper-Schrieffer (BCS) superconductor [19,20], the magnitude of κ_0/T is intimately related to the fine structure of the superconducting gap. Quantitatively, the theory states that $\kappa_0/T = [k_B^2/(3\hbar)] \times (v_F/v_2)(n/d)$ [20]. Here, v_F and v_2 are velocities of nodal quasiparticles normal and parallel to the Fermi surface, and $\frac{n}{d}$ is the stack density of CuO_2 planes. According to the theory, the magnitude of κ_0/T is universal in the sense that it does not depend on the scattering rate [19]. This prediction is valid in the clean limit, that is, when $\gamma \ll k_B T_c$, with γ being the impurity bandwidth. Experimentally, both in $YBa_2Cu_3O_{6.9}$ (Y-123) [14] and in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) [16], the magnitude of κ_0/T has been found to be independent of impurity concentration up to the highest scattering rates investigated for optimally doped samples. On the other hand, according to recent studies on La-214 [17,18] and on Y-123 [18], κ_0/T is a monotonously increasing function of doping concentration [17,18].

Figure 2(c) confirms the latter behavior in the case of Bi-2201. In the limited range of our exploration, the magnitude of κ_0/T increases with the increase in doping level. This allows us to determine the magnitude of κ_0/T in Bi-2201 at optimal-doping level ($p = 0.17$) to be

0.33 mW/K^2 cm. This value is more than twice the magnitude reported for Bi-2212 [15,16], which has a substantially higher T_c. This is not surprising, since κ_0/T is a zero-energy probe inversely proportional to the superconducting gap [18]. Now, it is tempting to forget that Bi-2201 is *not* in the clean limit (as defined a bove) and compute $v_F/v_2 = 35$, using the procedure already used for other cuprates [15,16,18]. Since v_2 is proportional to the angular slope of the gap at a nodal position, this number can be related to the magnitude of the superconducting gap assuming a regular d-wave angular dependence ($\Delta = \Delta_0 \cos 2\phi$). This yields $\Delta_0 = \hbar k_F v_2/2 = 16$ meV comparable with the magnitude reported by tunneling studies [21,22] (see Table I). Note that, while T_c is suppressed by a factor of 8 in Bi-2201, the associated reduction in the magnitude of the superconducting gap is considerably smaller, and the magnitude of κ_0/T appears to reflect this latter trend. This leads to an exceptionally high $\Delta/k_B T_c$ ratio in Bi-2201 ($\sim$15) [21], 7 times larger than the value expected for a d-wave BCS superconductor.

Normal state.—We now turn our attention to the issue of the validity or violation of the Wiedemann-Franz law, which states that the Lorenz number, $L = \kappa_N \rho_0/T$, should be equal to Sommerfeld's value:

$$L_0 = \frac{\pi^2}{3}\frac{k_B^2}{e^2} = 24.4 \times 10^{-9} V^2/K^2. \quad (1)$$

Here κ_N/T and ρ_0 are thermal conductivity and electric resistivity of the normal state in the $T = 0$ limit. Before presenting the data on heat conductivity in the normal state, let us note that in our samples the residual thermal conductivity in the *superconducting* state exceeds the magnitude of the thermal conductivity in the *normal* state expected by the magnitude of the resistivity [either $\rho(T_c)$ or ρ_0] and according to the WF law. In other words, $\kappa_0/T > L_0/\rho_0$. This surprising inequality was first reported in the case of underdoped La-214 [17]. In Bi-2201, as seen in Fig. 2(c), it persists at optimal doping, but gradually disappears with increasing p. In this context, a field-induced enhancement of κ_0/T, such as the one observed in optimally doped Bi-2212 [25], would lead to a strong violation of the WF law. In the underdoped La-214, on the other hand, κ_0/T decreases with the application of a magnetic field [26,27]

TABLE I. A comparison of two Bi-based cuprates at optimal doping level. κ/T is expressed in mW/K^2 cm units. Δ_0 was calculated using $v_F = 250$ km/s and $k_F = 0.7$ Å^{-1} obtained in angle-resolved photoemission spectroscopy studies on Bi-2212 [23].

Compound	T_c (K)	κ_0/T	$\frac{v_F}{v_2}$	Δ_0 (meV)	$\Delta_{\rm tunnel}$ (meV)
Bi-2212	89	0.15	19	30	~40 [24]
Bi-2201	11	0.33	35	16	12–15 [21,22]

As seen in Fig. 3, however, the application of a magnetic field, strong enough to destroy any trace of superconductivity in charge transport, has little effect on low-temperature thermal conductivity of Bi-2201. In the slightly overdoped sample ($p = 0.19$), the magnetic field leads to a slight increase in the residual linear term. No change in κ/T is observed for $H = 15$ T and $H = 20$ T. The few available data points for $H = 25$ T confirms that a reliable linear term for this field can be extracted from the data obtained at lower fields. Assuming that the magnetic field does not affect the slope of κ/T in the ballistic regime, we estimate $\kappa_N/T = 0.46 \pm 0.04$ mW/K^2 cm by extrapolating the $H = 20$ T data to $T = 0$ along a line parallel to the $H = 0$ slope. In the case of the optimally doped sample ($p = 0.17$), a magnetic field of 25 T leaves the thermal conductivity virtually unchanged in the explored temperature range. Thus, the zero-field extrapolation for this sample ($\kappa_0/T = 0.32 \pm 0.03$ mW/K^2 cm) may be considered as the magnitude of κ_N/T. As seen in the figure, for both samples, κ_N/T exceeds L_0/ρ_0. The excess is about 20(30)% for the $p = 0.19(0.17)$ sample.

In order to estimate our resolution in the verification of the WF law in a simple metal, we used the same setup to measure the low-temperature thermal and electric

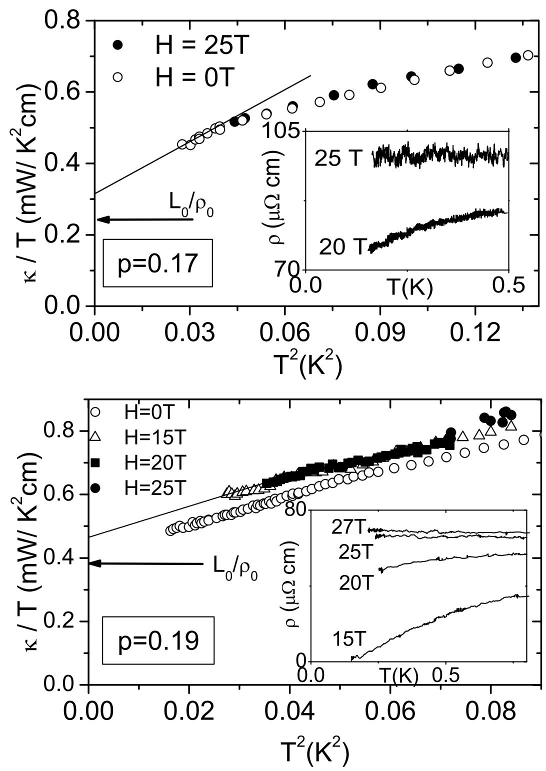

FIG. 3. Upper and lower panels: The effect of magnetic field on subkelvin thermal conductivity in two Bi-2201 samples with different doping levels. Solid lines represent the extrapolated low-temperature behavior and arrows show the expected WF magnitude. The insets display the resistivity data for the two samples.

conductivities of a 17 μm-diameter gold wire at $H = 0$ and $H = 25$ T [11]. The application of the magnetic field led to a threefold increase in ρ_0 and a concomitant decrease in κ/T of the gold wire. Using Coulomb blockade thermometry, we succeeded in verifying the WF law with a precision of 1(3)% at $H = 0$ (25 T) [11]. Thus, the deviation observed in Bi-2201 is much larger than our experimental precision on the absolute magnitude of κ/T.

Besides absolute thermometry, other sources of error may arise in the case of submillimetric and anisotropic samples. The geometric factor, assumed identical for κ and ρ in our analysis, may be different for electric and thermal transport. Since we did not observe any correlation between the magnitude of thermal conductivity and the width of gold electrodes, we can exclude the finite width of the contacts as a significant source of discrepancy. An eventual c-axis contamination of the presumably in-plane conductivity would lead to an overestimation of ρ_0. Moreover, as the electric transport is much more anisotropic than heat transport, the measured κ/T would be less affected by such a contamination. We estimate that, in the case of a $p = 0.17$ sample (with a thickness of 2.5 μm), this can lead to an error of 6% in the absolute magnitude of residual resistivity.

The sum of the three identified sources of experimental error (extrapolation to zero temperature, absolute thermometry, and overestimation of residual resistivity due to a c-axis contamination) yields an uncertainty of 17%. We can therefore conclude that for the $p = 0.17$ sample the Lorenz number exceeds Sommerfeld's value by a slight yet significant margin, that is $L = 1.3 \pm 0.2L_0$.

Prior to this work, compelling evidence for the validity of the WF law in the overdoped regime was reported for overdoped Tl-2201 ($p = 0.26$) [2] and for heavily overdoped La-214 ($p = 0.30$) [3]. Together with the detection of a purely T^2 temperature dependence of the resistivity in the latter compound, this seems to establish that the ground state in the overdoped limit is indeed a Fermi liquid. A previous study performed on an electron-doped cuprate at optimal-doping level pointed to a different conclusion [1]. Note, however, that in the latter experiment the extraction of κ_N/T was complicated by the presence of an intriguing downturn in thermal conductivity below 0.3 K. For temperatures above 0.3 K, Hill *et al.* extracted a κ_N/T which exceeded the expected WF value by a factor of 1.7 [1]. Our results do not suffer from the presence of this downturn which was also observed in overdoped La-214 [3,18]. They yield a κ_N/T, still larger than, but closer to, the WF value. Very recently, we have found that the slight deviation observed here is enhanced with underdoping and/or disorder [28]. This indicates that the slight departure from the WF law at optimal-doping level is not due to an experimental imperfection.

The outcome of this study has interesting implications for the debate on the origin of the anomalous transport properties of cuprates. In theories invoking electron fractionalization in cuprates [29], the zero-temperature excitations of the normal state are not Landau quasiparticles, and the WF law is not expected to be valid. In the case of a Luttinger liquid, for example, a strong violation of the WF law has been theoretically predicted [30]. On the other hand, if the anomalous properties of the normal state are due to the existence of a competing hidden order, then the validity of the WF law at $T = 0$ is still expected [31].

In summary, we have measured heat transport in the normal and superconducting state of Bi-2201. In the normal state, we have found a Lorenz number slightly but significantly larger than Sommerfeld's value.

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