Heat transport in $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$: departure from the Wiedemann-Franz law in the vicinity of the metal-insulator transition

Cyril Proust$^{1,2}$, Kamran Behnia$^3$, Romain Bel$^1$, Duncan Maude$^3$ and S. I. Vedeneev$^4$

$^1$Laboratoire de Physique Quantique (CNRS), ESPCI, 10 rue Vauquelin, 75231 Paris, France
$^2$ Laboratoire National des Champs Magnétiques Pulsés (CNRS-UPS-INSA), BP 14245, 31432 Toulouse, France
$^3$ Grenoble High Magnetic Field Laboratory (CNRS), BP 166, 38042 Grenoble, France
$^4$ P.N. Lebedev Physical Institute, Russian Academy of Sciences, 119991 Moscow, Russia

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We present a study of heat transport in the cuprate superconductor $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+\delta}$ at subkelvin temperatures and in magnetic fields as high as 25T. In several samples with different doping levels close to optimal, the linear-temperature term of thermal conductivity was measured both at zero-field and in presence of a magnetic field strong enough to quench superconductivity. The zero-field data yields a superconducting gap of reasonable magnitude displaying a doping dependence similar to the one reported in other families of cuprate. The normal-state data together with the results of the resistivity measurements allows us to test the Wiedemann-Franz (WF) law, the validity of which was confirmed in an overdoped sample in agreement with previous studies. In contrast, a systematic deviation from the WF law was resolved for samples displaying either a lower doping content or a higher disorder. Thus, in the vicinity of the metal-insulator cross-over, heat conduction in the zero-temperature limit appears to become significantly larger than predicted by the WF law.

Possible origins of this observation are discussed.

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I. INTRODUCTION

The study of subkelvin heat transport in high-$T_c$ cuprates has been a subject of considerable interest over the past few years. The pioneer work by Taillefer and co-workers resolved a finite linear term in the thermal conductivity of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6-\delta}$ (YBCO) in the zero-temperature limit. Subsequently, this experimental probe has been the object of a large number of experimental and theoretical investigations. It appears that these measurements have opened a new window on transport by the nodal quasi-particles of the superconducting state.

A number of remarkable findings have emerged. In agreement with theoretical predications for a d-wave superconductor, the zero-temperature thermal conductivity of optimally-doped cuprates was found to be universal in the sense that a strong variation of the scattering time of the quasi-particles due to disorder has little effect on the magnitude of the electronic thermal conductivity in the zero-temperature limit, $\kappa_0/T$. Moreover, the superconducting gap extracted from $\kappa_0/T$ has a nodal slope and a size comparable to what has been measured by other techniques. On the other hand, $\kappa_0/T$ was found to show a strong doping dependence. It decreases steadily as the Mott insulator is approached. If one assumes that $\kappa_0/T$ continues to inversely scale with the superconducting gap in the underdoped regime, this result points to a superconducting origin for the pseudogap. Finally, the field dependence of thermal conductivity has been another source of insight. In the optimally-doped cuprates, $\kappa_0/T$ was found to increase as a function of magnetic field providing an experimental confirmation of the Volovik excitations expected in a d-wave superconductor. In underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO), however, $\kappa_0/T$ decreases with magnetic field in the mixed state and is reminiscent of the metal-insulator transition observed by resistivity measurements in the normal state.

In principle, the study of thermal transport in the normal state of the cuprates allows to test what is generally believed to be a robust signature of a Fermi liquid, namely the Wiedemann-Franz (WF) law. According to this law, providing that collisions of electrons are elastic, the thermal and electrical conductivities are related by a universal constant.

$$\frac{\kappa}{\sigma T} = L_0$$

where $L_0 = 2.44 \times 10^{-8} \text{W} \text{Ω} \text{K}^{-2}$ is Sommerfeld’s value.

One obvious difficulty, in performing such a test, is to attain the normal state in the $T=0$ limit. The magnetic field needed to destroy the superconducting ground state in archetypal optimally-doped cuprates is simply too large. Therefore, attempts to test the validity of the WF law in various cuprates were all made in compounds where superconductivity is (for one reason or another) much weaker or absent. The first study, on the electron-doped $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ at optimal doping, led Hill et al.
to report a violation of the WF law for the first time in any metal. The most striking feature of the data was a vanishing of the electronic thermal conductivity both in the normal and in the superconducting states below 0.3K which is now believed to be a consequence of decoupling between electron and phonon thermal baths. As emphasized by Hill et al., the electronic thermal conductivity extracted above 0.3 K yielded \( \kappa/T \sim 1.7L_0 \). However, the presence of the extrinsic downturn hampered the solid establishment of such a violation of the WF law in the T=0 limit.

In a second study, Proust et al. provided compelling evidences for the validity of the WF law in overdoped Ti-2201 with an accuracy of a few percent. Nakamne et al. confirmed this validity in the case of heavily overdoped non-superconducting LSCO. Moreover, the latter study indicated that the downturn of thermal conductivity reported by Hill et al., is extrinsic as it was reproduced in a system displaying a Fermi liquid ground state. The observed validity of the WF law in overdoped cuprates is in conformity with the general belief that the ground state in this regime is indeed a Fermi liquid.

In this paper, we report on a study of heat transport in \( \text{Bi}_{2+\delta}\text{Sr}_{2-x}\text{CuO}_{6+\delta} \), a cuprate, which, even at optimal doping, presents an unusually low \( T_c \) (~10 K) and a relatively accessible \( H_{c2} \). In a previous communication on the first part of these measurements, we reported that for an optimally-doped sample, \( \kappa/\sigma T = 1.3L_0 \). This small departure from the Wiedemann-Franz law appeared to be nevertheless significant as it was larger than the experimental error. Here, we present new data which shows that the departure is even larger in two other samples and systematically increases with underdoping and/or disorder. The picture emerging from this study is a pronounced violation of the WF law in the vicinity of the metal-to-insulator transition in cuprates. What is observed is a roughly two-fold excess of heat conductivity as originally-reported in PCCO by Hill et al. for \( T>0.3\)K. Our observation remains robust down to the lowest temperatures explored and is not contaminated by the extrinsic downturn present in PCCO. Moreover, our study of the superconducting state in \( \text{Bi}_{2}\text{Sr}_{2}\text{CuO}_6 \) is in conformity with features reported in other cuprates, indicating that heat transport in this member of the cuprate family does not fundamentally differ from the others.

II. THE MEASUREMENT AND ITS PRECISION

In-plane thermal conductivity was measured with a standard two-thermometer-one-heater setup which allows to measure the in-plane electrical resistivity under the same conditions. A number of zero-field measurements reported here were performed at the ESPCI in Paris. However, in order to measure subkelvin thermal conductivity in a Bitter/polyhelix magnet at the Grenoble High Magnetic Field Laboratory (GHMFL), we developed a new experimental set-up. The water-cooled resistive magnet generates mechanical vibrations, a part of which is inevitably transmitted to the thermometers coupled to the sample. In order to overcome this problem, our set-up containing the sample and thermometers is placed inside a vacuum chamber, which can be introduced into the mixing chamber of a commercial top-loading dilution refrigerator with a relatively large cooling power (~300 \( \mu W \) at 100 mK).

The second technical challenge was to accurately measure the temperature since the magnetoresistance of the ruthenium oxide thermometers is far from negligible. For this purpose, we used a coulomb blockage thermometer (CBT), a primary thermometer know to show no variation with magnetic field. This thermometer has been used in situ in order to calibrate in a magnetic field, the RuO\(_2\) sensors used to measure local temperature of the sample.

In order to estimate the experimental resolution, we have verified the WF law in a gold wire by measuring thermal conductance and electrical resistance in zero magnetic field and for \( H=25 \) T. As seen in Fig. 1, the thermal conductivity is purely electronic and therefore a linear function of temperature. The magnitude of the linear term can be compared to what is expected according to the WF law (solid lines in Fig. 1). Both at zero magnetic field and \( H=25 \) T, the magnitude of \( \kappa/T \) is very close to \( L_0/R \), where \( R \) is the measured resistance of the wire. The application of a magnetic field leads to a threefold decrease of \( \kappa/T \), reflecting the positive magnetoresistance of gold in this temperature range. The discrepancy between \( \kappa/T \) and \( L_0/R \) is 1% (3%) for \( H=0 \) (\( H=25 \) T), giving an estimation of experimental precision. Since the electrical resistance of the gold wire is

![FIG. 1: Thermal conductance of a gold wire for \( H=0 \) (open circle) and for \( H=25 \) T (solid squares) compared to the magnitude expected by the WF law (solid lines).](image-url)
comparable to the resistance of the normal state of the cuprate samples measured in our investigation, this also provides a verification of the absolute value of thermal conductivity obtained in our study and shows that the thermal leak of our set-up is negligible.

The major source of uncertainty when determining the absolute value of $\kappa$ and $\sigma$ is due to the geometric factors which are about $\pm 10\%$. In principle, the verification of the WF law should not suffer from this uncertainty, since no geometric factor enters in Eq. 1 and the same contacts are used for measuring electrical voltage and temperature. In practice, the geometric factor could be slightly different for electric and thermal transport, if the width of gold pads evaporated on the sample is not negligible over the distance between the two voltage (thermometer) contacts. However, we did not observe any correlation between the magnitude of thermal conductivity and the width of gold electrodes. Additional sources of uncertainty come from an eventual c-axis contamination of the in-plane conductivity, which would lead to an overestimation of $\rho_{\|}$ and the extrapolation of linear term of the thermal conductivity at $T=0$. The sum of the identified sources of experimental error yields an uncertainty of $\approx 20\%$ for the verification of the WF law.

### III. SAMPLES, DOPING LEVEL AND DISORDER

We have studied five single crystals of $B_{\delta+z}S_{2-x}R_{2-z}CuO_{6+\delta}$. They were grown in a gaseous phase in closed cavities of a KCl solution melt as detailed elsewhere. Typical dimensions of the crystals are $(2-10)\times(400-800)\times (600-900)\ \mu m^3$. Four gold pads are evaporated onto the surface of the samples with a typical contact resistance of about 1 ohm.

Starting from the insulating phase $B_{\delta+z}S_{2}R_{2}CuO_{6}$, there are two possibilities to add carriers in the $CuO_2$ planes. One may change the amount $\delta$ of excess oxygens in $BiO$ planes or substitute $Sr^{2+}$ ions by trivalent ions, such as $La^{3+}$ or excess of $Bi^{3+}$. Due to the difficulty of changing the oxygen content in a controlled way, $as-grown$ crystals were used in this study. The variation of $T_c$ is set by changing the $Bi$ and $Sr$ contents.

The maximum $T_c$ found in $B_{\delta+z}S_{2-x}R_{2-z}CuO_{6+\delta}$ was found to be $\approx 10\ K$ in agreement with previous studies. This is much lower than the $T_c$ of 33 K in the La-doped ($B_{\delta+z}S_{2-x}R_{2-z}La_xCuO_{6+\delta}$) system. The very low level of $T_c$ in La-free Bi-2201 has already been recently addressed by a careful study of Eisaki et al., who probed the impact of $Sr$ substitution by ions with different radius on the physical properties of Bi-2201. They suggest that cation disorder, particularly at the $Sr$ site, strongly affects the maximum attainable $T_c$. On the basis of the ionic radii shown by Ahrens, they correlate the size of the ionic radius of $Sr^{2+}$ ($1.12\ A$), $La^{3+}$ ($1.14\ A$) and $Bi^{3+}$ ($0.96\ A$) with the magnitude of $T_c$. The mismatch between the ionic radii of $Sr^{2+}$ and $Bi^{3+}$ causes additional lattice distortions and may account for the low $T_c$ in $B_{\delta+z}S_{2-x}R_{2-z}CuO_{6+\delta}$. It is worth to notice that Shannon found different ionic radius values since it depends on the coordinates and its surrounding in the lattice.

Excess oxygen in $BiO$ planes would also engender a random potential in the $CuO_2$ planes but in a less controlled way. Indeed, Ono and Ando have already noticed that the magnitude of the resistivity at $T_c$ can vary from sample to sample at the same doping level because of inhomogeneous oxygen concentration in the sample. During our study, we have noticed that with aging and thermal cycle, our underdoped samples are not stable and evolve. This is illustrated by the data shown in Fig. 2. Bottom panel shows the temperature dependence of the resistivity of the as-grown sample UD3 (solid line) and during a second measurement performed a few months after (dotted line). The corresponding low-temperature thermal conductivity is displayed in the top panel of the same figure. Note that during the first measurement (solid triangles) performed at GHMFL, the data points stop at a relatively higher temperature ($\approx 0.19\ K$). The change in thermal conductivity at this temperature is just comparable with experimental resolution. As seen in the

![Graphical representation](image_url)

**FIG. 2:** Upper panel: Thermal conductivity of sample UD3 measured a first time (solid triangles) and a second time using another set-up three months later (open squares). Lower panel: Temperature dependence of the resistivity of the same sample measured under the same conditions. Solid (dotted) line is the first (second) measurement.
lower panel, however, the electrical resistivity at $T_c$ has increased by $\sim 20\%$. Assuming that subkelvin thermal conductivity does not depend on impurity concentration (which is the case of cuprates at optimal doping level), this data suggests that the change in $T_c$ and resistivity with time are mostly due to an increase in the level of disorder and not a change in the carrier concentration (which would have left a stronger signature on the thermal conductivity). In order to minimize the contamination of our study by this evolution, whenever we compare electrical and thermal conductivities of a given sample, we use the thermal and electrical data measured at the same time. Optimally-doped (OP) and overdoped (OD) samples were found to be more stable and no significant change in their electrical and/or thermal conductivities was detected after thermal cycling and aging.

An accurate determination of the doping level, $p$, in the five samples used in this study (and listed in Table I) is not easy. We used the value of $T_c$ as the relevant parameter to estimate the doping level. Ando et al.\textsuperscript{32} have reported that in La-doped Bi-2201 the variation of $T_c$ with the doping level is much faster than that found in other families of cuprates. The usual “Bell shape” curve can be expressed as:

$$\frac{T_c}{T_{c_{max}}} = 1 - a(p - p_{opt})^2$$ \hspace{1cm} (2)

While in the “universal” expression for the doping dependence of the critical temperature\textsuperscript{a} $a = 82.6$, the data in La-doped Bi-2201\textsuperscript{32} yields $a = 275$. We have used the latter value, together with $T_{c_{max}} = 10.2K$ and $p_{opt} = 0.17$. A supplementary check on the doping level of our samples was performed by measuring the Hall coefficient, $R_H$ in two other samples of the same batch with a $T_c$ and resistivity indicative of optimal doping. As expected, the magnitude of the Hall coefficient normalized by the volume of the elementary cell, $R_{He} / V_0$, was found to be close to the expected value for an optimally-doped cuprate\textsuperscript{23} Taking into account all these considerations, the accuracy of the doping level determined for each sample is estimated to lie in a margin of $\pm 0.01$.

IV. CHARGE TRANSPORT

Fig. 3(a) shows the temperature dependence of the resistivity of the five Bi-2201 samples. The magnitude of the resistivity at $T_c$ varies from 0.05 m$\Omega$ cm for the overdoped (OD) sample to 0.3 m$\Omega$ cm for the most underdoped (UD) sample, in good agreement with recent investigation of charge transport in Bi-2201 at different doping levels.\textsuperscript{22} Note that 0.3 m$\Omega$ cm translates to the Ioffe-Regel parameter $k_F l \approx 11$, which corresponds to a metallic regime. Fig. 3(b) shows the resistivity versus temperature of sample UD3 at different magnetic fields. The inset presents the magnetoresistivity measured around 0.3 K which shows that resistive transition is complete at H=25 T. As revealed by the careful study in ref.\textsuperscript{34} the resistivity of underdoped sample show an upward curvature in presence of a magnetic field below $T_c$, but it saturates at very low temperature. The same trend is observed in the two underdoped samples. Fig. 3(c) displays the temperature dependence of the resistivity of four samples measured at 25 T for testing the WF law. For samples UD2 and UD3, the value of the residual resistivity at $H=25$ T is slightly higher than the value at $T_c$, but saturates to a well-defined value below $T=1$ K.\textsuperscript{57} This is an indication that the doping level of the underdoped samples lies close to the metal-insulator transition but it stays in the metallic side.

V. SUPERCONDUCTING STATE

Before addressing the test of WF law in Bi-2201, we begin by presenting the thermal conductivity of the superconducting state, in the absence of magnetic field.

The lower panel of Fig. 4 displays the temperature dependence of thermal conductivity of the five Bi-2201 samples at zero magnetic field. The data is plotted as $\kappa / T$ versus $T^2$ in order to distinguish the phonon contri-
TABLE I: Physical characteristics of the Bi-2201 samples in this study: $T_c$, $p$ (number of carriers per Cu atom), residual linear term in the thermal conductivity as well as the gap maximum $\Delta_0$ deduced from Eq. 6.

| Sample | $T_c$ (K) | $p$ | $\kappa_0/T$ (mW/K$^2$ cm) | $\Delta_0$ (meV) |
|--------|----------|----|----------------|-----------------|
| OD     | 9.2      | 0.189±0.01 | 0.4±0.04 | 7.1±0.7 |
| OP     | 10.2     | 0.17±0.01  | 0.33±0.03 | 8.6±0.9 |
| UD1    | 7.5      | 0.139±0.01 | 0.19±0.02 | 14.9±1.5 |
| UD2    | 7.7      | 0.14±0.01  | 0.15±0.02 | 18.8±1.9 |
| UD3    | 8.1      | 0.143±0.01 | 0.26±0.03 | 10.8±1.2 |

contribution to the thermal conductivity. Indeed, at very low temperatures, when the scattering of phonons becomes ballistic (e.g. limited by the surface of the sample), the total thermal conductivity can be written as:

$$\kappa(T) = aT + bT^3$$

where the linear term is the electronic contribution. In a $d$-wave superconductor, this corresponds to heat transport by nodal quasiparticles. The second term represents the phonon contribution. Hence, plotting $\kappa/T$ vs. $T^2$, the linear term can be obtained by extrapolating the data with a straight line to the $T=0$ axis. The magnitude of the linear terms $\kappa_0/T$ versus doping level is shown in the upper panel of Fig. 4. It can be noticed that $\kappa_0/T$ increases when the doping level increases, in agreement with previous studies on other families of cuprate superconductors and Bi2212 with much higher $T_c$s and a considerably larger superconducting gap. It is also twice larger than the value ($\sim 0.16$ mW/K$^2$cm) reported for La-doped Bi-2201 at the same doping level. The difference between La-free and La-doped Bi-2201 could be intrinsic and a consequence of the higher $T_c$ (38 K compared to 10 K) in the latter system. However, one cannot exclude an experimental artefact. Indeed, an anomalous downturn is present in the data reported for La-doped Bi-2201. In other words, below a certain sample-dependent temperature, $\kappa/T$ suddenly appears to decrease faster as a function of $T^2$. Such a downturn, known to contaminate thermal conductivity measurements at very low temperatures would lead to an underestimation of $\kappa_0$ in La-doped Bi-2201.

BCS theory, when applied to a $d$-wave superconductor, associates the linear term in thermal conductivity to the fine structure of the superconducting gap at nodes. This association can be written as:

$$\kappa_0 = \frac{k_B^2 n v_F}{3\hbar d v_2}$$

Here $v_F$ and $v_2$ are the velocities of nodal quasiparticles normal and parallel to the Fermi surface, respectively.

FIG. 4: a): Thermal conductivity at low temperature for different samples plotted as $\kappa/T$ versus $T^2$. The dotted lines represent linear extrapolations to $T=0$. b): Doping dependence of the linear term of the thermal conductivity extrapolated to $T=0$ (squares).

and $n/d$ is the number of CuO$_2$ planes per unit cell. In the clean limit, when $h\gamma < k_BT_c$, this linear term is universal in the sense that it does not depend on the scattering time. Assuming a pure $d_{x^2-y^2}$ symmetry for the superconducting gap and given that

$$v_2 = \frac{1}{\hbar k_F} \left. \frac{d\Delta}{d\phi} \right|_{\text{node}}$$

the magnitude of the superconducting gap is directly related to the magnitude of the linear term

$$\Delta_0 = \frac{k_B^2 n k_F v_F}{6 a \kappa_0 / T}$$

Using the typical Fermi surface parameter for Bi$_2$Sr$_2$CaCu$_2$O$_{8}$ (Bi-2212) namely $k_F=0.7$ Å along the nodal direction and $v_F = 2.5 \times 10^7$ cm/s, and $n/d = 2/c$ with $c = 24.6$ Å for Bi-2201, we obtain $\Delta_0 \sim 8.6 \pm 0.9$ meV at optimal doping. It should be compared to the value for other cuprates at optimum doping estimated using the same method: namely, 30 meV for Bi-2212 and 50 meV for YBCO. It is noteworthy that while $T_c$ of La-free Bi-2201 is reduced by almost one order of magnitude.
compared to Bi-2212 the magnitude of the gap is reduced by a much smaller factor. It is instructive to compare the value deduced from thermal conductivity to what has been directly measured using tunnelling ($\Delta_{\text{tunnel}} \approx 12-15$ meV\textsuperscript{35,36}) and ARPES ($\Delta_{\text{ARPES}} \approx 10 \pm 2$ meV\textsuperscript{22}).

One should not forget that in Bi-2201, the impurity bandwidth $\hbar \gamma$ is not negligible compared to $k_B T_c$. Indeed, using the Drude formalism for resistivity, $\rho = m/e^2 \tau$, and the plasma frequency, $\omega_p^2 = ne^2/\epsilon_0 m$ and given that $\rho(T_c) \approx 100 \mu \Omega \ cm$, $\hbar \omega_p = 8300 \ cm^{-1}$ at optimal doping, we can estimate the impurity bandwidth in the unitary limit $\hbar \gamma = 0.63 \sqrt{\Delta_0/2\tau} \approx 5$ meV, which is a sizeable fraction of the superconducting gap. Since any correction to the universality should increase the magnitude of the linear term\textsuperscript{20} the intrinsic linear term (i.e. not renormalized by disorder) is actually smaller than the measured one and therefore the actual magnitude of the superconducting gap maybe higher than 8.6 meV.

It is instructive to compare our Bi-2201 samples to highly overdoped Tl$_2$Ba$_2$CuO$_{4+\delta}$\textsuperscript{21} with $T_c \approx 15$ K, for which the linear term in the superconducting state is 1.41 mW/K$^2$ cm and translates to $\Delta_0 \approx 2.1$ meV, comparable to the BCS prediction $2.14k_B T_c \approx 2.8$ meV. In Bi-2201, around optimal doping, the magnitude of the superconducting gap deduced from thermal conductivity is about five times larger than the BCS prediction. This difference has been interpreted by assuming that the gap seen in thermal conductivity is related to the pseudogap\textsuperscript{22}. In the d-density-wave (DDW) scenario for example, the pseudogap has $d_{x^2-y^2}$ symmetry with linear dispersion near the node. Thermal conductivity is universal provided that the chemical potential is neglected and the nesting is perfect. The linear term probes thus a gap which is not purely superconducting but can be expressed as $\Delta = \sqrt{\Delta_1^2 + \Delta_2^2}$ where $\Delta_1$ and $\Delta_2$ are the order parameters of DDW and $d$-wave superconductivity, respectively.

VI. TEST OF THE WIEDEMBERG-FRANZ LAW

Let us now turn our attention to the verification of the WF law. A comparison of Subkelvin thermal conductivity at zero field and 25 T is shown in Fig. 5 for four samples which were measured at high magnetic field. Note that this data correspond to measurements performed on as-grown samples. For sample OD (Fig. 5a), the application of the magnetic field leads to a slight, yet visible increase in thermal conductivity. At optimal doping (Fig. 5b), the thermal conductivity is almost identical for normal and superconducting states. However, for the underdoped samples UD2 (Fig. 5c) and UD3 (Fig. 5d), thermal conductivity decreases with the application of magnetic field as it does in underdoped LSCO\textsuperscript{6,16}. In the latter case, the field-induced decrease in thermal conductivity was interpreted as a field-induced thermal metal-insulator transition presumably as a consequence of a competing order with superconductivity such as spin-density-wave\textsuperscript{39}. The existence of such competing order has been theoretically predicted in the phase diagram of cuprates when disorder plays a prominent role\textsuperscript{40}. Sutherland et al.\textsuperscript{14} report that, in contrast to LSCO, underdoped YBCO, for a doping level of $\delta \approx 0.33$ (corresponding to the onset of superconductivity), is a thermal metal. In other words, it does not display a detectable field-induced decrease in thermal conductivity. This conclusion is not shared by Sun et al.\textsuperscript{42} who report a metal-insulator transition around $\delta = 0.45$. The level of disorder in Bi-2201 is certainly closer to LSCO than to ultra-clean YBCO\textsuperscript{43}. Therefore, it is not surprising that, underdoped Bi-2201 displays a field-induced decrease in $\kappa_0/T$ in analogy with LSCO.

A second feature of the data presented in Fig. 5 is the upward deviation of any zero-temperature extrapolation of the normal-state thermal conductivity compared to what is expected according to the WF law. As seen in the figure, such a deviation becomes striking in the underdoped samples. In Fig. 6 we have plotted the Lorenz
number \( L = \kappa \rho_0 / T \) normalized by \( L_0 \) versus \( T^2 \), where \( \rho_0 \) is the normal state resistivity (measured at 25T, using the data of Fig. 3c). Dashed line shows the value expected according to the WF law. For the OD sample \( p=0.19 \), we recover the WF law within a margin 5\%. This result is in agreement with the behavior observed for overdoped Tl-2201 \((p=0.26)\). For the OP sample, a magnetic field of 25 T leaves thermal conductivity unchanged for the explored temperature range. Thus, we have used the zero-field extrapolation as the residual normal state thermal conductivity, which gives a Lorenz ratio \( L=1.3L_0 \), significantly larger our uncertainty. It can be noticed that the deviation of the WF law when \( T \to 0 \) becomes more pronounced for underdoped samples. Indeed, the \( T=0 \) extrapolation of the thermal conductivity in the normal state of sample UD2 \((p=0.14)\) leads to a Lorenz ratio \( L=1.9L_0 \). For sample UD3 \((p=0.143)\), the extrapolation to \( T=0 \) leads to a violation of the WF law by a factor of 3. However, given the lack of low temperature data for this sample, this value could be overestimated.

VII. DISCUSSION

In the main panel of Fig. 7(a), the Lorenz ratio normalized by \( L_0 \) is plotted versus carrier concentration for all Bi-2201 samples in this study. There is also a sketch of the superconducting dome given by Eq. 2 with the La-doped Bi-2201 parameter. In the inset of Fig. 7(a), we summarized the available data on the validity of the WF law in cuprate superconductors. In addition to our Bi-2201 data (full squares), we put data on LSCO \((open square)\), Tl-2201 \((open circle)\) and PCCO \((open triangle)\).

These results indicate that the WF law is verified in the overdoped side of the phase diagram. Indeed, it has been now verified in three families of cuprate superconductors. A departure starts to develop at optimal doping. It becomes particularly pronounced at a doping level \( p \sim 0.14 \) lying close to the metal-to-insulator cross-over. The shaded area marks the cross-over from metal-to-insulator in La-doped Bi-2201 and LSCO. The horizontal line is the WF expectation. The shaded area represents the “insulating” ground state associated with a logarithmic divergency of the resistivity, which is reported to occur for \( p \leq 0.12 \) both in La-doped and in La-Free Bi-2201. Obviously, the WF law is not relevant for an insulator lacking delocalized fermions. However, as seen in Fig. 3(c), the samples presented in this study are not insulators and their resistivity display almost no temperature dependence below 1K.

According to our current understanding, the observed violation of the WF law in underdoped Bi-2201 samples cannot be attributed to any known experimental artefact.
The magnitude of the departure ($L/L_0 \geq 2$) is well above our experimental resolution. It is reproducible and becomes systematically larger with the increase in disorder and/or underdoping. While the underdoped samples may host an inhomogeneous distribution of oxygen content as discussed above, this is expected to affect the transport of heat and charge in the same way. In the absence of any plausible scenario linking an excess of heat conductivity to extrinsic effects or to a macroscopic inhomogeneity, we should consider the possible microscopic origins of such a violation.

The first class of available scenarios are based on spin-charge separation. A strong violation of the WF law is predicted in the case of a Luttinger liquid. Indeed, in a one-dimensional interacting electron system, quasiparticles are replaced by collective excitations of charge (without spin) and spin (without charge) moving independently and at different velocities. Since the electrical current probes only the charge excitations, while the thermal current is sensitive to both charge and spin excitations, there is an excess in thermal conductivity compared to electric conductivity. An upward deviation from the WF law is thus expected. A similar violation of the WF law is expected in theories invoking electron fractionalization in cuprates. We note, however, that other experimental signatures expected in case of such a fractionalization have not been detected.

Another class of models are those invoking the breakdown of the Fermi liquid in the vicinity of a Quantum Critical Point (QCP). The existence of a hidden order such as a d-density-wave has been proposed in order to explain the pseudogap phenomena. Analysis of the transport properties of such a state indicates that the WF law should remain intact in the zero-temperature limit. To a QCP, however, one may expect the emergence of non-Fermi liquid properties which may include a violation of the WF law. We note, however, that a study of the WF law in CeNi$_2$Ge$_2$, a heavy-fermion compound lying close to a QCP, did not find any detectable departure from the WF law.

Until very recently, it was widely believed that the WF law is a robust property of any Fermi liquid. In particular, Castellani and co-workers established the validity of the WF law in interacting disordered electron system up to the metal-insulator transition. However, this issue has been reexamined recently by three independent groups, who all suggest the violation of the WF law in a disordered conductor with interacting electrons. Roughly speaking, this violation arises because the Coulomb interaction leads to an additional scattering at low temperatures which impedes charge transport more efficiently. In such a context, the expected deviation from the WF law is positive and scales with $1/k_F^2$. Therefore, for the most underdoped Bi-2201 sample, the expected deviation is $L/L_0 \sim 1.1$. Such a deviation is an order of magnitude smaller than observed experimentally $L/L_0 \sim 2$. This quantitative disagreement should however be put into context. The origin of the logarithmic divergence of resistivity in cuprates which occurs for surprisingly high values of $k_F$ is still far from understood. If this last line of speculation happens to be the relevant one, then disorder, more than doping level, would be the key parameter. Fig. 7(b) presents the Lorenz ratio normalized by $L_0$ versus the residual resistivity ratio (RRR), that is the ratio between the room temperature resistivity and the normal state resistivity at $H=25$ T and $T\rightarrow 0$. The latter is a common parameter for quantifying the level of disorder. As seen in the figure, the magnitude of $L/L_0$ is in excellent correlation with the decrease in RRR. This correlation appears to be even more robust than the one observed between $L/L_0$ and the doping level displayed in the upper panel.

VIII. CONCLUSION

We have studied low-temperature thermal transport in several crystals of Bi-2201 with different doping levels. In the superconducting state, the residual linear term of thermal conductivity steadily increases with the increase in the doping level as previously reported for other families of the cuprates. The application of the magnetic field leads to an increase in thermal conductivity in overdoped regime and a decrease in the underdoped regime. A departure from the WF law appears for optimal doping and becomes more pronounced for underdoped samples. This provides experimental evidence for the violation of the WF law in the vicinity of metal-insulator transition in cuprates.

IX. ACKNOWLEDGEMENT

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Note that the margin of verification in this sample is some-
what smaller than what was reported in ref. 24
above 15 T, we used the H=20 T data for estimating L
becomes field-independent
κ/T
Note that the resistivity curve of sample UD2 in Fig. 3(c)
plays a higher absolute resistivity.
For this sample, we had only a few data points for H=25 T.
Since they indicated that
plays a higher absolute resistivity.
Fig. 3(a) corresponds to a second measurement and dis-
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Corresponds to a first measurement whereas the curve in
Fig. 3(a) corresponds to a second measurement and dis-
plays a higher absolute resistivity.
Note that the value calculated in ref. 24 is overestimated by a factor 2
For this sample, we had only a few data points for H=25 T.
Since they indicated that κ/T becomes field-independent above 15 T, we used the H=20 T data for estimating L0.
Note that the margin of verification in this sample is somewhat smaller than what was reported in ref. 24