

## Delocalized Fermions in Underdoped Cuprate Superconductors

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Low-temperature heat transport was used to investigate the ground state of high-purity single crystals of the lightly doped cuprate  $\text{YBa}_2\text{Cu}_3\text{O}_{6.33}$ . Samples were measured with doping concentrations on either side of the superconducting phase boundary. We report the observation of delocalized fermionic excitations at zero energy in the nonsuperconducting state, which shows that the ground state of underdoped cuprates is a thermal metal. Its low-energy spectrum appears to be similar to that of the  $d$ -wave superconductor, i.e., nodal. The insulating ground state observed in underdoped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  is attributed to the competing spin-density-wave order.

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Electrons in cuprates adopt a remarkable sequence of ground states as one varies the density of charge carriers. When the electron density in the  $\text{CuO}_2$  planes of a cuprate material is exactly 1.0 per Cu atom in the plane, the material is a Mott insulator with static long-range antiferromagnetic order, and the electrons are localized on their sites by strong Coulomb repulsion. This electronic gridlock can be relaxed by removing electrons from the planes, a charge-transfer process induced by chemical substitution away from the planes. This doping process adds  $p$  holes per Cu atom in the planes, and at high carrier density yields a normal metal with the basic signatures of a Fermi liquid. At intermediate density, it is a superconductor with  $d$ -wave symmetry, but the nature of the underdoped phase that lies between the insulator and the superconductor is one of the central puzzles of the field. It is known to be characterized by a pseudogap, and is thought to be an exotic state of matter [1–4]. As one moves into this enigmatic underdoped phase by adding carriers to the Mott insulator, a key question remains: does the onset of superconductivity coincide with the onset of hole mobility? In  $\text{V}_2\text{O}_3$  [5] and 2D organic conductors [6], pressure studies have answered this question in the affirmative: the electron system goes directly from insulator to superconductor, with no intermediate phase.

Attempts to address this issue in the cuprates have thus far focused almost entirely on the LSCO system [7], which is known to be intrinsically disordered. To probe this question in the absence of disorder, we turn to the cleanest cuprate available and investigate whether holes are mobile or not by measuring their ability to transport heat, as  $T \rightarrow 0$ . The technique of heat conduction has several advantages: (1) it is sensitive only to mobile excitations, (2) it can distinguish between fermionic and bosonic excitations, and (3) it probes the bulk of a sample, unaffected by possible inhomogeneities at the surface. In this Letter, we present a

comparative study of heat transport in two cuprate materials,  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (YBCO) and  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO). The effect of doping is investigated by comparing samples of each material with doping on either side of  $p_{\text{SC}}$ , the critical doping for the onset of superconductivity. Our main finding is the observation of delocalized fermionic excitations in the nonsuperconducting state of YBCO ( $p < p_{\text{SC}}$ ) at  $T \rightarrow 0$ . This shows that upon doping, a clean cuprate can first go from Mott insulator to thermal metal before it turns into a superconductor, meaning that holes (or spins) can be mobile without forming a condensate of Cooper pairs. In contrast, in the LSCO system, such delocalized low-energy excitations are not observed in the nonsuperconducting state [8,9], showing that excitations are either localized (by the stronger disorder) or gapped, possibly by spin-density-wave (SDW) order.

YBCO single crystals of the highest available purity were used, for which there is ample evidence of extremely long electronic mean free paths [10], estimated to be approximately 2 orders of magnitude longer [11] than in the best LSCO crystals. The oxygen content of an ultra-clean YBCO crystal [12] was set to be near  $y = 6.33$  so that  $p$  would lie close to  $p_{\text{SC}}$ . The concentration of holes doped into the  $\text{CuO}_2$  planes depends on the degree of oxygen order in the CuO chains, and as a result increases as a function of time spent annealing at room temperature [13]. The sample was first measured directly after growth, before any room-temperature annealing took place. At this stage it was nonsuperconducting (no sign of a transition in resistivity down to  $T = 80$  mK) so that  $p < p_{\text{SC}}$ . The same sample was remeasured after spending 2 days annealing at room temperature, after which it was a superconductor with  $T_c = 0.1$  K, where we define  $T_c$  by  $\rho = 0$ . After 3 weeks of further annealing,  $p$  increased such that  $T_c = 6$  K. For YBCO, we use the well-known empirical relation,  $T_c/T_c^{\text{max}} = 1 - 82.6(p - 0.16)^2$  [11], to define

hole concentration. This yields  $p = 0.051$  and  $0.054$  for 2 days of annealing and 3 weeks of annealing, respectively. We estimate the nonsuperconducting state (no annealing) to have  $p \sim 0.048$  by extrapolating the hole concentration backwards in time on a logarithmic plot [13]. For LSCO, two samples are used: one nonsuperconducting ( $T_c = 0$ ) with  $x = 0.05$  ( $p < p_{SC}$ ) and one superconducting ( $T_c = 5$  K) with  $x = 0.06$  ( $p > p_{SC}$ ), where we simply use  $p = x$ , the Sr concentration.

We investigate the ground state conductivity by measuring heat transport down to 80 mK, which allows for a reliable extrapolation to  $T = 0$ . We begin with nonsuperconducting samples ( $p < p_{SC}$ ). In Fig. 1, the thermal conductivity  $\kappa$  of the nonannealed YBCO sample is compared to that of a previously measured LSCO sample [9] with  $x = 0.05$ . The data is plotted as  $\kappa/T$  vs  $T^{\alpha-1}$  to provide a straightforward way of extrapolating to  $T = 0$ , and obtain the residual linear term  $\kappa_0/T$ . The absence of a residual linear term ( $\kappa_0/T = 0$ ) indicates the absence of fermionic carriers as in an insulator or a fully gapped ( $s$ -wave) superconductor. A finite (nonzero) value can be attributed unambiguously to delocalized fermionic excitations. In either case, the slope of the curves is a measure of the phonon conductivity [11]. In YBCO, a distinct linear term is observed, of magnitude  $\kappa_0/T = 46 \pm 8 \mu\text{W K}^{-2} \text{cm}^{-1}$ , much larger than that obtained for an undoped crystal [11] ( $y = 0.0$ ) where  $\kappa_0/T = 0 \pm 1 \mu\text{W K}^{-2} \text{cm}^{-1}$ . By con-

trast, the LSCO sample yields a vanishingly small linear term of  $\kappa_0/T = 3 \pm 1 \mu\text{W K}^{-2} \text{cm}^{-1}$ , just as in the undoped ( $x = 0.0$ ) material [9], indicating a ground state devoid of delocalized carriers for all  $p < p_{SC}$  (i.e.,  $x < 0.05$ ). This observation points to a fundamental difference between the two systems: YBCO is a thermal metal, LSCO is a thermal insulator. Having uncovered delocalized fermions in a lightly-doped cuprate with no long-range superconducting order, we explore some of their basic properties: how do they compare to the  $d$ -wave nodal quasiparticles of the superconducting state (at  $p > p_{SC}$ )? How do they respond to a magnetic field?

We begin by comparing the nonsuperconducting phase below  $p_{SC}$  with the coherent superconducting state, above  $p = p_{SC}$ . The dependence of  $\kappa_0/T$  on doping is shown in Fig. 2, combining present and previous data [11]. We note that the data is qualitatively similar to the zero-field data reported for  $y > 6.45$  by Sun *et al.* [14], although their conclusions differ from ours [15]. In a  $d$ -wave superconductor, nodal quasiparticles give rise to a finite  $\kappa_0/T$ , the magnitude of which is governed entirely by their Dirac energy spectrum. Indeed, in the universal limit, where the residual linear term is independent of impurity concentration, the value of  $\kappa_0/T$  only depends on the ratio  $v_F/v_2$ , where  $v_F$  and  $v_2$  are the quasiparticle velocities perpendicular and parallel to the Fermi surface, respectively [17]:

$$\frac{\kappa_0}{T} = \frac{k_B^2}{3\hbar} n \left( \frac{v_F}{v_2} + \frac{v_2}{v_F} \right). \quad (1)$$

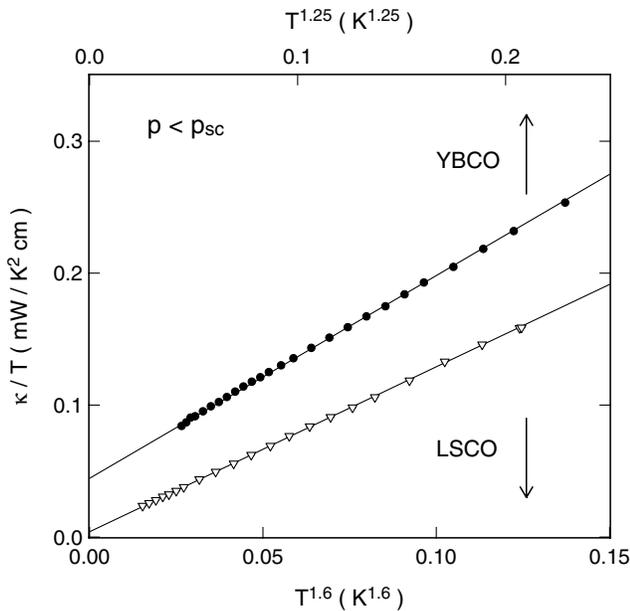


FIG. 1. Thermal conductivity of underdoped cuprates YBCO and LSCO. Both have a hole concentration  $p$  close to, but less than  $p_{SC}$ , the critical concentration for the onset of superconductivity. The YBCO sample shows a sizable residual linear term  $\kappa_0/T$ , indicating the presence of delocalized fermionic carriers of heat. The LSCO sample shows a vanishingly small value of  $\kappa_0/T$ , consistent with an insulating state.

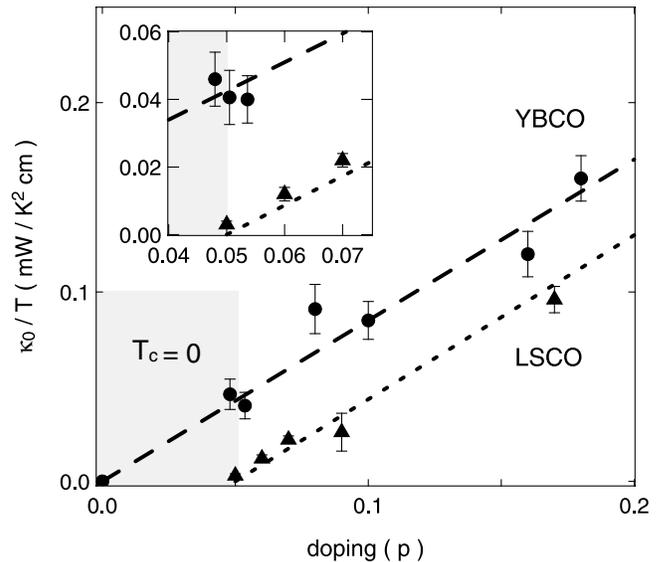


FIG. 2. Residual thermal conductivity as a function of carrier density  $p$  for YBCO (circles) and LSCO (triangles). The fermionic heat conductivity decreases with decreasing  $p$  in both cases, but at  $p_{SC}$  it goes to zero in LSCO while it remains finite in YBCO. Dashed lines are guides to the eye. Inset: Zoom on region close to  $p_{SC}$ .

Here  $n$  is the number of  $\text{CuO}_2$  planes per unit cell of height  $d$ . Previous measurements have shown that this formalism works remarkably well [18]: in optimally-doped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  BSCCO, thermal conductivity directly gives  $v_F/v_2 = 19$ , while a ratio of  $v_F/v_2 = 20$  is obtained from independent measurements of  $v_F$  and  $v_2$  by angle-resolved photoemission spectroscopy (ARPES).

It is straightforward to use such measurements to extract an estimate of the superconducting gap maximum, assuming a simple  $d$ -wave gap of the form  $\Delta = \Delta_0 \cos 2\phi$ , so that  $2\Delta_0 = \hbar k_F v_2$ . The value one obtains for the gap in YBCO in this manner tracks the value measured by ARPES well into the underdoped regime [11,19]. This shows that the overall decrease in  $\kappa_0/T$  with underdoping is caused by a monotonically increasing gap. For the highly underdoped YBCO samples measured here, the linear term of approximately  $40 \mu\text{W K}^{-2} \text{cm}^{-1}$  implies a gap maximum of 160 meV, which suggests that the in-plane exchange coupling energy  $J$  of the Mott insulator, estimated to be 125 meV [20], sets the magnitude of  $\Delta_0$ . Note that this type of analysis is only valid in the universal limit (i.e., when the scattering rate is small compared to  $\Delta_0$ ), a condition which was indeed verified in YBCO at both  $y = 6.9$  and  $6.5$  [11].

Two important points emerge from Fig. 2. First, the monotonic decrease in  $\kappa_0/T$  with underdoping observed in YBCO persists smoothly through the critical point at  $p = p_{\text{SC}}$ : there is no detectable change in the conductivity of YBCO in going from the  $d$ -wave superconductor into the nonsuperconducting phase. Indeed, within error bars the residual linear term in the nonannealed state (with  $p$  just below  $p_{\text{SC}}$ ),  $\kappa_0/T = 46 \pm 8 \mu\text{W K}^{-2} \text{cm}^{-1}$  is identical to the fully-annealed state (with  $p > p_{\text{SC}}$  and  $T_c = 6$  K),  $\kappa_0/T = 40 \pm 7 \mu\text{W K}^{-2} \text{cm}^{-1}$ . Given that the residual linear term is solidly understood as arising from nodal quasiparticles in the superconducting state, its seamless evolution into the nonsuperconducting state below  $p_{\text{SC}}$  suggests that a nodal spectrum is also a characteristic of the thermal metal phase.

The second important conclusion one may draw from Fig. 2 is that YBCO appears to be qualitatively different from LSCO. While in the former the quantum phase transition at  $p_{\text{SC}}$  has no impact on the conductivity of the electron system, in the latter it corresponds to a (thermal) metal-insulator transition. Indeed in LSCO,  $\kappa_0/T$  goes to zero precisely where superconductivity disappears. The very same situation was observed to occur as a function of applied magnetic field, for  $p > p_{\text{SC}}$ : the transition from thermal metal ( $d$ -wave superconductor) to insulator was found to be simultaneous with the suppression of superconductivity, occurring right at the resistive upper critical field  $H_{c2}$ , for a LSCO sample with  $x = 0.06$  [9].

The difference between YBCO and LSCO may lie in the greater amount of disorder found in LSCO, which would cause the nonsuperconducting state of LSCO near  $p = p_{\text{SC}}$

to be an insulator (thermally and electrically). However, if LSCO were merely a disordered version of YBCO, it is hard to see why the metal-to-insulator transition would be pinned to the onset of superconductivity (at  $p_{\text{SC}}$ ). The latter fact points instead to another explanation, namely, a scenario of competing phases where the other phase (e.g., with SDW order) is insulating, for example, as a result of having a small gap at the nodes [21]. Along these lines, recent neutron scattering studies [22,23] of underdoped LSCO in a magnetic field have revealed a field-induced increase in static SDW order. This happens in parallel with the field-induced decrease in conductivity [9]. The induced magnetic order may well serve to either gap out or localize the fermionic excitations responsible for heat transport as  $T \rightarrow 0$ .

Let us now examine the response of YBCO to a magnetic field applied perpendicular to the  $\text{CuO}_2$  planes. In a  $d$ -wave superconductor, the superfluid flow around each vortex causes a Doppler shift of the quasiparticle energies and thus an increase in the zero-energy density of states. This should lead to an increase in thermal conductivity. In YBCO near optimal doping, an increase in  $\kappa_0/T$  was observed to be on the order of a factor 2 in 10 T or so [24]. In LSCO, a similar increase is seen at optimal doping, but for  $p < 0.1$ ,  $\kappa_0/T$  was found to decrease, as mentioned above and reproduced for  $p = 0.06$  in Fig. 3. This decrease is a signature of the thermal metal-to-insulator transition at  $H = H_{c2}$ . In YBCO, no such decrease is observed for  $p$  close to  $p_{\text{SC}}$  (or anywhere; see [15]). In Fig. 3 one can see that the thermal conductivity of the YBCO sample is in fact entirely unaffected by field. After 2 days of annealing, the

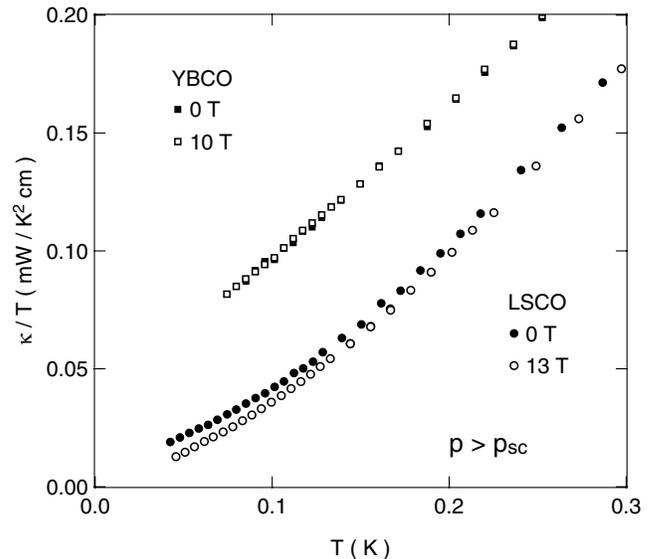


FIG. 3. Temperature dependence of thermal conductivity for  $p > p_{\text{SC}}$  in YBCO and LSCO, in both the superconducting state ( $H = 0$ ) and the normal state ( $H > H_{c2}$ ). The doping  $p$  is just above  $p_{\text{SC}}$ ,  $p = 0.051$  with  $T_c = 0.1$  K in YBCO and  $x = p = 0.06$  with  $T_c = 5$  K in LSCO.

sample has  $T_c = 0.1$  K ( $\rho = 0$ ) and 10 T is enough to suppress superconductivity entirely. The extrapolated linear term does not change:  $\kappa_0/T = 43 \pm 7 \mu\text{W K}^{-2} \text{cm}^{-1}$  in 10 T, compared to  $40 \pm 7 \mu\text{W K}^{-2} \text{cm}^{-1}$  in zero field. The same field independence is observed with either  $T_c = 0$  (unannealed) or with  $T_c = 6$  K. The conclusion is, therefore, that in YBCO near  $p_{SC}$  the thermal conductivity does not change across the phase boundary, whether one reaches the nonsuperconducting state by decreasing  $p$  at fixed  $H = 0$  or by increasing  $H$  at fixed  $p > p_{SC}$ .

This is reminiscent of previous spectroscopic studies (ARPES [25] and tunnelling [26]) which found the gap in underdoped cuprates to persist largely unchanged as the temperature was increased from below to above  $T_c$ . The observation of this “pseudogap” above  $T_c$  has been interpreted as the persistence of pairing amplitude (gap) once long-range superconducting order has been destroyed by thermal fluctuations of the phase [27]. Within such an interpretation, the fact that our measurements are done essentially at  $T = 0$  would imply a quantum (rather than thermal) disordering of the phase with increasing magnetic field or decreasing doping. What our study shows is that this putative phase disordering would leave the system in a ground state with fermionic elementary excitations (in this connection see [28]). Beyond this particular interpretation, several theoretical models have been proposed for the pseudogap state of underdoped cuprates [3,29,30]. It remains to be seen which of the proposed states support both a  $d$ -wave-like gap at high energies and fermionic excitations down to zero energy.

In conclusion, we have presented evidence to show that the nonsuperconducting state of pure cuprates in the underdoped regime of the phase diagram is a thermal metal. The associated low-energy fermionic excitations have a heat conductivity that evolves seamlessly from the superconducting phase, which suggests they have a nodal spectrum akin to that of the  $d$ -wave superconductor. In other words, as holes are doped into the cuprate Mott insulator, a thermally metallic ground state is first reached before the onset of phase-coherent superconductivity. We propose this as the generic scenario of clean cuprates. Note that it is not realized in the case of LSCO, which instead shows insulating behavior, most likely caused by the presence of a competing SDW order.

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