Universal Heat Conduction in $YBa_2Cu_3O_{6.9}$

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The thermal conductivity of $YBa_2Cu_3O_{6.9}$ was measured at low temperatures in untwinned single crystals with concentrations of Zn impurities from 0% to 3% of Cu. A linear term $\kappa_0/T = 0.19$ mW K^{-2} cm^{-1} is clearly resolved as $T \rightarrow 0$, and found to be virtually independent of Zn concentration. The existence of this residual normal fluid strongly validates the basic theory of transport in unconventional superconductors. Moreover, the observed universal behavior is in quantitative agreement with calculations for a gap function of d-wave symmetry. [S0031-9007(97)03618-1]

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The theory of quasiparticle transport in unconventional superconductors, developed over the last decade, has remained largely untested. A novel feature that arises when the superconducting gap function has nodes for certain crystal directions is the existence of quasiparticles at $T = 0$. This residual normal fluid is a consequence of impurity scattering, even for low concentrations of nonmagnetic impurities (see [1,2], and references therein). Its presence, which should dominate the conduction of heat and charge at $T \ll T_c$, has yet to be firmly established [3], and its properties have never been investigated. For certain pairing states, with appropriate gap topology and symmetry, an appealing phenomenon is predicted to occur: quasiparticle transport should be independent of scattering rate as $T \rightarrow 0$. This universal limit, first pointed out by Lee [4] for the case of a d-wave gap in two dimensions, is the result of a compensation between the growth in normal fluid density with increasing impurity concentration and the concomitant reduction in mean free path.

In this Letter, we report the first observation of universal transport in a superconductor. Our study of heat conduction in the high-T_c cuprate $YBa_2Cu_3O_{6.9}$ provides a solid validation of the basic theory of transport in unconventional superconductors and insight into the nature of impurity scattering in the cuprates. It also supports strongly an identification of the gap function as having d-wave symmetry.

The thermal conductivity $\kappa(T)$ was measured between 0.05 and 1 K, for a current along the a axis of five single crystals: four untwinned crystals of $YBa_2(Cu_{1-x}Zn_x)_3O_{6.9}$ and one crystal of $YBa_2Cu_3O_{6.0}$. The latter was obtained by full deoxygenation via annealing at 800 °C in helium gas for 64 h; it is insulating, with $\rho_a(100\text{ K}) = 42.7\ \Omega$ m. x is the nominal concentration of Zn, achieved by mixing in ZnO powder at the start of the growth process in the atomic ratio Zn:Cu::$1.5x$:$1 - x$, for $x = 0$, 0.006, 0.02, and 0.03. The experimental technique and the sample preparation are described elsewhere [5,6]. The resistive T_c is given in Table I. The uncertainty on the geometric factor is at most $\pm 10\%$, 10%, 20%, 5%, and 10% for the $x = 0$ ("pure"), 0.6%, 2%, 3%, and deoxygenated ("deox") samples, respectively.

The a-axis resistivity is linear in temperature above 130 K [6], and a fit to $A + BT$ yields the values in Table I. Zn substitution has two effects: it reduces T_c and it increases A. At low concentration, both effects are linear, and $dT_c/dA = -0.5$ K/$\mu\Omega$ cm, in agreement with data on twinned crystals (e.g., [7]). Concentrations of Zn from 0% to 3% correspond to a large range of scattering rates, but to a modest level of pair breaking: adding 3% Zn suppresses T_c by only 20%. Given that the inelastic scattering term B is independent of x, the impurity scattering rate $\Gamma = 1/2\tau_0$ may be estimated via the residual resistivity $\rho_0 = m^*/ne^2\tau_0$:

$$\Gamma_\rho(x) = (\omega_p^2/8\pi)[\rho_0(x = 0) + A(x) - A(0)], \quad (1)$$

where $\omega_p = \sqrt{4\pi ne^2/m^*}$ is the Drude plasma frequency and $\rho_0(x = 0)$ is the resistivity of the pure crystal at $T = 0$. The latter is estimated via the microwave conductivity, from which the mean free path is known to increase by $\simeq$100 in going from 100 K to $\simeq$10 K in

TABLE I. Sample characteristics for the four untwinned a-axis crystals of $YBa_2(Cu_{1-x}Zn_x)_3O_{6.9}$. x is the nominal zinc concentration and T_c is the superconducting transition temperature. A and B are extracted from a linear fit of the resistivity ($130 < T < 200$ K). The scattering rate Γ_ρ is estimated via the resistivity using Eq. (1) with $\omega_p = 1.3$ eV and $\rho_0(x = 0) = 1\ \mu\Omega$ cm.

x (%)	T_c (K)	A ($\mu\Omega$ cm)	B ($\mu\Omega$ cm K^{-1})	Γ_ρ/T_{c0} ($\hbar/k_B$)
pure	93.6	−14.3	0.95	<0.014
0.6	89.2	−6.0	1.00	0.13
2	80.0	12.9	0.94	0.4
3	74.6	22.9	1.07	0.54

high-quality untwinned crystals [8]. Since $\rho_a(100\ \text{K}) \simeq 75\ \mu\Omega$ cm, then $\rho_0(x = 0) < 1\ \mu\Omega$ cm. With $\omega_p = 1.3$ eV (a axis) [9], one gets the scattering rates listed in Table I, in units of $T_{c0} = T_c(x = 0)$. Note that *3% of Zn causes a 40-fold increase in* Γ.

In order to use $\kappa(T)$ as a probe of quasiparticle behavior, the phonon contribution must be extracted reliably. This can be done only by going to temperatures sufficiently low that the phonon conductivity κ_{ph} has reached its well-defined asymptotic T^3 dependence, given by

$$\kappa_{\text{ph}} = \frac{1}{3}\,\beta\langle v_{\text{ph}}\rangle\Lambda_0 T^3, \qquad (2)$$

where β is the phonon specific heat coefficient, $\langle v_{\text{ph}}\rangle$ is a suitable average of the acoustic sound velocities, and Λ_0 is the temperature-independent maximum phonon mean free path. In nonmagnetic insulators, acoustic phonons are the only carriers of heat at low temperature and Eq. (2) is well verified, with $\langle v_{\text{ph}}\rangle = v_L(2s^2 + 1)/(2s^3 + 1)$ in single crystals, where $s = v_L/v_T$ is the ratio of longitudinal to transverse velocities [10]. In high-quality crystals, $\Lambda_0 = 2\bar{w}/\sqrt{\pi}$, where $\bar{w}$ is the (geometric) mean width of a rectangular sample [10].

The simplest way of investigating the phonon contribution in $YBa_2Cu_3O_y$ is to remove all electronic carriers by setting $y \simeq 6.0$. (Note that antiferromagnetic magnons are not expected to contribute at $T < 1$ K, since the acoustic spin-wave gap in $YBa_2Cu_3O_{6.15}$ is $\simeq$100 K [11].) The thermal conductivity of such an insulating crystal is shown in Fig. 1 (triangles). As seen from the linear fit, $\kappa/T = a + bT^2$ below about 0.15 K, with $a = 0$ and $b = 14\ \text{mW}\,\text{K}^{-4}\,\text{cm}^{-1}$. The first question of interest is: what happens when electronic carriers are introduced? The answer is provided by the thermal conductivity of a well-oxygenated crystal, also shown in Fig. 1 (circles): *electronic carriers contribute a definite linear term to* $\kappa(T)$. Applying the same fit as before yields $a = 0.19\ \text{mW}\,\text{K}^{-2}\,\text{cm}^{-1}$ and $b = 17\ \text{mW}\,\text{K}^{-4}\,\text{cm}^{-1}$.

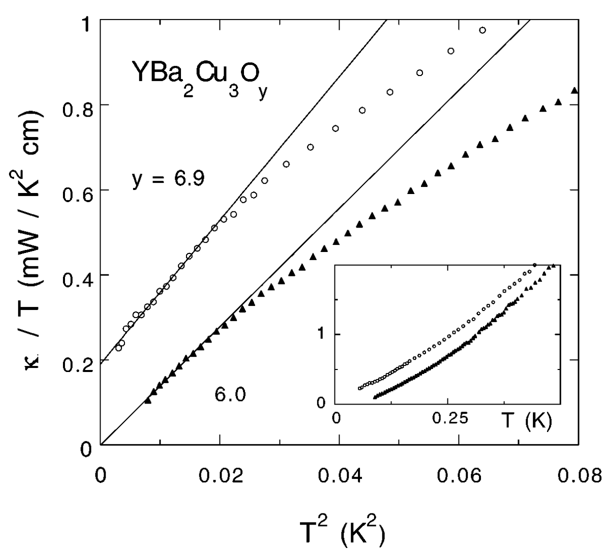

FIG. 1. a-axis thermal conductivity of the two $YBa_2Cu_3O_y$ crystals, one superconducting ($y = 6.9$; circles) and one insulating ($y = 6.0$; triangles). Main panel: κ/T vs T^2; lines are fits to $a + bT^2$ for $T < 0.15$ K. Inset: κ/T vs T.

It must be emphasized that such an analysis is sound only when applied to the asymptotic regime for κ_{ph}. To confirm that this is indeed the case for $T < 150$ mK in the insulating crystal, note that $a = 0$ *and* the magnitude of the cubic term is right; i.e., it corresponds to a maximum mean free path Λ_0 dictated by the mean crystal width $\bar{w}$. Indeed, from Eq. (2) using $\beta = 0.3$–$0.4\ \text{mJ/K}^4$ mole [12,13] and $\langle v_{\text{ph}}\rangle = 4000$ m/s ($v_L \simeq 6000$ m/s, $v_T \simeq 3700$ m/s [14]), $\Lambda_0 = 270$–$360\ \mu\text{m} = 2\bar{w}/\sqrt{\pi}$ (see Table II). (Note that β and $\langle v_{\text{ph}}\rangle$, given here for $y \simeq 6.9$, could be slightly different for $y \simeq 6.0$ [13,14].) So the phonon mean free path in the $y = 6.0$ sample unambiguously reaches its maximum, boundary-limited value at $\simeq$0.15 K. It is then reasonable to expect a very similar *phonon* behavior in the $y = 6.9$ sample, given its nominally identical crystalline quality and surface quality, and its comparable dimensions. This is nicely borne out by the κ/T data in Fig. 1: the only difference between the two curves ($y = 6.9$ and 6.0) is a rigid offset. In such a well-defined context, the appearence of a linear term upon introducing electronic carriers is conclusive evidence for the existence of zero-energy quasiparticles in $YBa_2Cu_3O_{6.9}$ and, as a result, it confirms a key feature of the basic theory of transport in unconventional superconductors [1,2,4,15–18]. In this connection, earlier claims of a residual electronic linear term in κ of $YBa_2Cu_3O_{7-\delta}$ were inconclusive, being all based on the same analysis as used here but applied to arbitrary temperature regimes (for a review, see [19]).

Having established the existence of a residual normal fluid in $YBa_2Cu_3O_{6.9}$, the next question is that of universality. This is addressed by looking at concentrations of Zn such that Γ ranges from $<0.014T_c$ up to $0.54T_c$. The thermal conductivity of $YBa_2(Cu_{1-x}Zn_x)_3O_{6.9}$ is shown in Fig. 2, where it is apparent that κ is unaffected by the variation in Γ at $T \simeq 0.1$ K, where the heat is carried predominently by quasiparticles (cf. Fig. 1). In other words, *transport by the residual normal fluid is universal.*

The $T \rightarrow 0$ limit of κ/T is obtained from a fit to $a + bT^2$ limited to $T < 150$ mK, as applied earlier, which yields the values for $a = \kappa_0/T$ and b listed in Table II. Note that the ratio $\Lambda_0/(2\bar{w}/\sqrt{\pi}) \simeq 1$ for all crystals, proving that the asymptotic phonon regime was reached in all cases. (The somewhat larger ratio for the pure sample is intriguing—further work is needed to elucidate this.) As seen from a plot of κ_0/T versus Γ, shown in Fig. 3, these values are consistent with a universal linear term of $0.19\ \text{mW}\,\text{K}^{-2}\,\text{cm}^{-1}$. Note, however, that the error bars on the values of a and b in Table II are fairly large, because they combine uncertainties on the geometric factors (largest for the rather short 2% sample) and on the fit, which is limited to a small temperature range

TABLE II. Parameters used in fitting κ/T to $a + bT^2$, where $a = \kappa_0/T$ is the electronic residual linear term and $b = \kappa_{ph}/T^3$ is the asymptotic phonon T^3 term. $\bar{w}$ is the mean sample width and Λ_0 is calculated from Eq. (2) using $\beta = 0.3-0.4$ mJ/K^4 mole and $\langle v_{ph} \rangle = 4000$ m/s.

Sample (%)	$\bar{w}$ (μm)	κ_0/T (mW K^{-2} cm^{-1})	κ_{ph}/T^3 (mW K^{-4} cm^{-1})	$\sqrt{\pi}\,\Lambda_0/2\bar{w}$
Pure	252	0.19 ± 0.03	17 ± 2	1.2−1.6
0.6%	242	0.17 ± 0.04	11 ± 2	0.8−1.0
2%	177	0.25 ± 0.07	7 ± 3	0.7−0.9
3%	238	0.20 ± 0.05	8 ± 3	0.6−0.8
Deox	315	0.00 ± 0.01	14 ± 2	0.8−1.0

(smallest for the 3% sample). One way of eliminating the uncertainty on the geometric factor is to use the resistivity data obtained with the same contacts. Indeed, by fixing $B = 1.03\ \mu\Omega\,\mathrm{cm\,K^{-1}}$ for all samples, thereby imposing the reasonable constraint that the inelastic scattering is not affected by small levels of Zn, one can correct κ_0/T by multiplying it by $B(x)/1.03$. This yields the following corrected values: 0.17 ± 0.01, 0.17 ± 0.02, 0.23 ± 0.02, and 0.21 ± 0.04 mW K^{-2} cm^{-1}, for $x = 0\%$, 0.6%, 2%, and 3%, respectively. These are plotted in the inset of Fig. 3 versus the similarly corrected Γ_ρ. The corrected plot with its smaller error bars no longer allows for a constant linear term: there is a small but definite upward slope, with a minimum growth of 30% over the range of Γ_ρ and a maximum growth of 55%. From this we conclude that while the residual linear term is universal, in the sense that a tenfold increase in Γ (from $0.014T_c$ to $0.13T_c$ in going from $x = 0\%$ to 0.6%) leaves κ_0/T unchanged, at larger Γ there is a slight increase, reaching approximately 40% at $\Gamma/T_c \simeq 0.6$.

Let us now compare our results with the theory of heat transport in unconventional superconductors [15–18]. The first point to emphasize is that universality is expected only for special gap functions with appropriate topology and symmetry. This is the case for a pairing state of $d_{x^2-y^2}$ symmetry, with line nodes at azimuthal angles $\phi = m\pi/4$ ($m = 1, 3, 5, 7$). The $T = 0$ limit of κ/T along the x (or a) direction is [15,16]

$$\frac{\kappa_{00}}{T} = L_0\sigma_{00} \rightarrow \frac{L_0 n e^2}{m^*}\,\frac{2\hbar}{\pi S} = \frac{\hbar k_B^2 \omega_p^2}{6e^2}\,\frac{1}{S}\,, \qquad (3)$$

where σ_{00} is the universal limit of charge conductivity [4,16], $L_0 = (\pi^2/3)(k_B/e)^2$ is the Sommerfeld value of the Lorenz number, and $S = |d\Delta(\phi)/d\phi|_{\rm node}$ is the slope of the gap at the node [16]. The topology of the excitation gap right at the node [e.g., $\Delta(\phi) \sim \phi - \pi/4$] determines universality and then the slope S sets the magnitude of κ_{00}/T. Note that a gap function of the right topology but of s-wave symmetry will *not* in general show universal behavior, so that our observation of a universal κ_0/T is strong support for a gap of d-wave symmetry.

A quantitative comparison with the theory reinforces this conclusion. In the simplified case of the standard

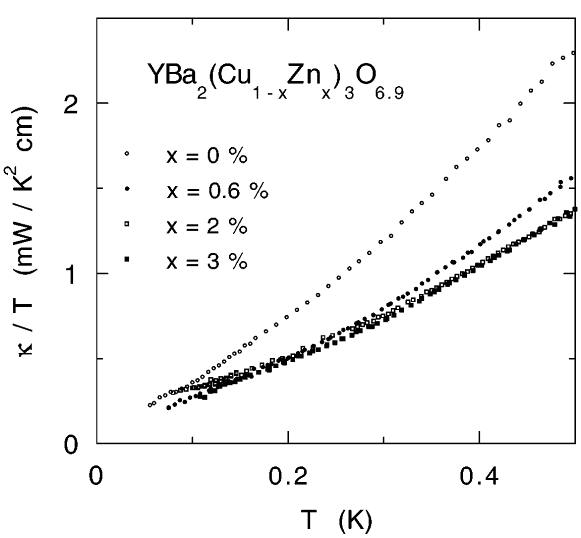

FIG. 2. a-axis thermal conductivity of the four Zn-doped crystals, plotted as κ/T vs T.

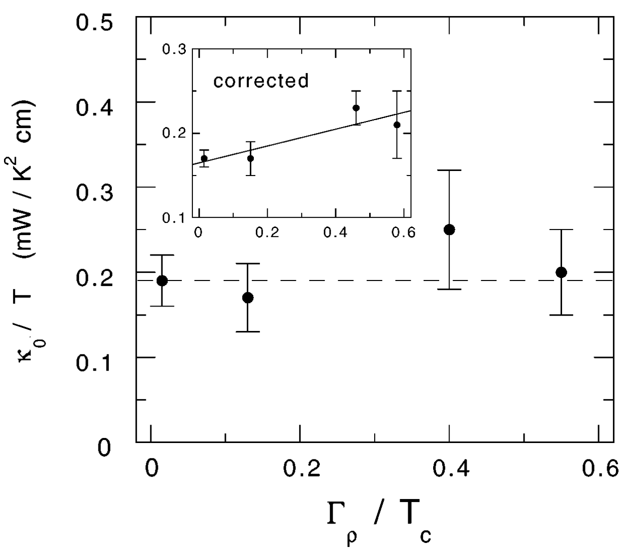

FIG. 3. Residual linear term vs scattering rate for the four crystals of $YBa_2(Cu_{1-x}Zn_x)_3O_{6.9}$; the dashed line indicates a constant at 0.19 mW K^{-2} cm^{-1}. Inset: same, but with corrected values (see text); the solid line is a least-squares fit.

d-wave gap $\Delta_0 \cos(2\phi)$, $S = 2\Delta_0$. Using available estimates of $\hbar\omega_p$ and the gap maximum Δ_0, respectively equal to 1.3 [9] and 20 meV [20], one gets

$$\frac{\kappa_{00}}{T} = 0.09 \text{ mW K}^{-2}\text{ cm}^{-1}, \qquad (4)$$

which is remarkably close to the measured value of 0.19 mW K^{-2} cm^{-1}. Given that the real gap will have more structure than a simple $\cos(2\phi)$ dependence, the factor of 2 discrepancy suggests that it actually rises from the node half as fast as in the simple model. This in no way detracts from the conclusion that a (generalized) *d-wave gap is in excellent quantitative agreement with the universal heat conduction observed in $YBa_2Cu_3O_{6.9}$.*

The second point to consider in a comparison with the theory is the fact that universality is achieved only when $\hbar\gamma \ll \Delta_0$, where $\hbar\gamma$ is the bandwidth of impurity bound states responsible for the zero-energy excitations [16]. The bandwidth grows with Γ in a way which depends very strongly on the scattering phase shift δ_0. It is largest in the limit of unitarity scattering, $\delta_0 = \pi/2$, where $\hbar\gamma \sim \sqrt{\pi\Delta_0\hbar\Gamma/2}$ [16]. For the pure and 3% samples, with $\Gamma_\rho/T_{c0} = 0.014$ and 0.54, this gives $\hbar\gamma/\Delta_0 \simeq 0.1$ and 0.6, respectively (for $\Delta_0 \simeq 20$ meV $= 2.5k_BT_{c0}$). Thus we expect deviations from universality for the samples with high Zn doping. Quantitatively, the dependence of κ_{00}/T on Γ was calculated by Sun and Maki [15], who find a monotonic increase, which gets to be a factor of 1.9 at $\Gamma/T_{c0} = 0.54$ (see also Ref. [17]). Such a large increase is incompatible with the data (see Fig. 3). On the other hand, a 40% growth in the residual linear term, consistent with the data, would agree with the calculation if $\Gamma \simeq \Gamma_\rho/2$, namely, $0.3T_{c0}$ for the 3% sample instead of $0.54T_{c0}$. Interestingly, this is the Γ one deduces self-consistently from the theory [21], based on the measured T_c suppression. Note, however, that accounting for a smaller Γ in terms of a smaller "effective" ω_p^2 in Eq. (1) leads to an even smaller κ_{00}/T from Eq. (3).

These minor discrepancies notwithstanding, one of the main implications of the good agreement with the theory is that impurity scattering in the cuprates is well described by a phase shift very close to $\pi/2$ [16], something which has been assumed often but rarely verified. Nonetheless, a proper interpretation of the data should include the possibility of a small departure from the unitarity limit [18]. This would lower γ, making it easier to satisfy the condition $\hbar\gamma \ll \Delta_0$, and possibly to account for the weak variation in κ_0/T.

The present results have implications for other properties of $YBa_2Cu_3O_{6.9}$, such as specific heat [12,13] and microwave conductivity [22]. It has not yet been possible to probe the residual normal fluid reliably via these properties, but the upper bounds imposed by the data so far are consistent with the behavior predicted on the basis of the thermal conductivity data reported here.

In summary, we presented the first observation of universality in the transport properties of a superconductor. A residual linear term $\kappa_0/T = 0.19$ mW K^{-2} cm^{-1} is clearly resolved in the thermal conductivity of $YBa_2Cu_3O_{6.9}$ and attributed to electronic carriers. The observation of this residual normal fluid is a powerful validation of the basic theory of impurity scattering in unconventional superconductors. The fact that κ_0/T is universal, i.e., virtually unaffected by changes in the impurity scattering rate, strongly confirms the gap as having d-wave symmetry. However, from the magnitude of κ_0/T, it appears that the gap rises more slowly at the nodes than described by the standard function $\Delta_0 \cos(2\phi)$ with $\Delta_0 = 2.5k_BT_{c0}$.

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