

Transport in Ultraclean $\text{YBa}_2\text{Cu}_3\text{O}_7$: Neither Unitary nor Born Impurity Scattering

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The thermal conductivity of ultraclean $\text{YBa}_2\text{Cu}_3\text{O}_7$ was measured at very low temperature in magnetic fields up to 13 T. The temperature and field dependence of the electronic heat conductivity show that two widespread assumptions of transport theory applied to unconventional superconductors fail for clean cuprates: impurity scattering cannot be treated in the usual unitary limit (nor indeed in the Born limit), and scattering of quasiparticles off vortices cannot be neglected. Our study also sheds light on the long-standing puzzle of a sudden onset of a “plateau” in the thermal conductivity of Bi-2212 versus field.

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Since 1985, the theory of transport in unconventional superconductors has been dominated by the ubiquitous assumption that impurity scattering must be treated in the unitary limit ($\pi/2$ phase shift) [1]. The aim of this Letter is to test this assumption in the simplest and most reliable context available, namely, that of the cuprate material $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO), for which the superconducting gap structure is firmly established and straightforward, with $d_{x^2-y^2}$ symmetry over an approximately cylindrical Fermi surface. We do this by measuring heat transport in ultraclean single crystals that have a scattering rate one order of magnitude lower than in previous studies. This allows us to reliably resolve the intrinsic temperature dependence of the electronic thermal conductivity.

The pivotal result of transport theory is the universal limit of conductivity, whereby the ability of a superconductor to carry heat as $T \rightarrow 0$ is independent of either the concentration of scattering centers or the strength of the scattering potential (i.e., phase shift). The universal limit was first observed in YBCO [2] and then confirmed in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (Bi-2212) [3], as well as in the p -wave superconductor Sr_2RuO_4 [4]. It is only by going beyond the universal limit that one can test the assumption of unitary scattering. The increase in conductivity with temperature T or applied magnetic field H is expected to depend strongly on scattering phase shift δ [5,6]. The main finding of the present study is that the electronic thermal conductivity increases with T much faster than could ever be expected from unitary scattering. The high degree of order in the present crystal also reveals unambiguously the dominance of vortex scattering over impurity scattering even at modest fields. This will shed light on the long-standing puzzle of a sudden onset of a plateau observed previously in the thermal conductivity of Bi-2212 versus field [7,8].

The thermal conductivity κ was measured using a single-heater–two-thermometer method. The heat current was supplied along the a axis of the sample, and

the magnetic field applied parallel to the c axis. The measurements were made in a dilution refrigerator by varying the temperature from 0.04 K to > 0.7 K at fixed magnetic field. The samples were field cooled by cycling to $T > 100$ K before changing the field. The error in the absolute value of the conductivity is estimated to be approximately 10%. The relative error between temperature sweeps at different fields is of order 1%.

The single crystal platelet of YBCO used in this study has dimensions $1.0 \times 0.5 \text{ mm}^2$ and $25 \mu\text{m}$ thick. It was grown in a BaZrO_3 (BZO) crucible [9], which results in crystals with extremely high chemical purity (99.99%–99.995%) and a high degree of crystalline perfection as compared with crystals grown in Y_2O_3 -stabilized ZrO_2 (YSZ) crucibles. The sample was detwinned at 250°C under uniaxial stress, followed by a 50 day annealing process at 350°C , resulting in oxygen chains with less than 0.7% vacancies. This level of oxygen doping, $x = 6.99$, is slightly above that for maximal T_c (93 K), resulting in a marginally lower $T_c = 89$ K. Four electrical contacts were applied using silver epoxy fired at 350°C for 1 h, giving typical contact resistances of 200 m Ω at 4.2 K.

The high purity of our sample can be established from its thermal conductivity at high temperature. A low defect level leads to a larger peak in κ below T_c , as noted by Zhang *et al.* [10]. In the inset in Fig. 1, we show the thermal conductivity for this sample as compared to a detwinned YBCO sample with $x = 6.95$ grown in an YSZ crucible. The approximate doubling in peak height can be attributed to an order of magnitude decrease in the intrinsic disorder level [11] (see also [12]).

The main panel of Fig. 1 shows the temperature dependence of the thermal conductivity of the high-purity (BZO) sample at zero field and in applied fields of 0.8 and 13 T. The thermal conductivity is the sum of electronic and phononic contributions: $\kappa = \kappa_e + \kappa_{\text{ph}}$. The residual linear term κ_0/T , obtained by extrapolating

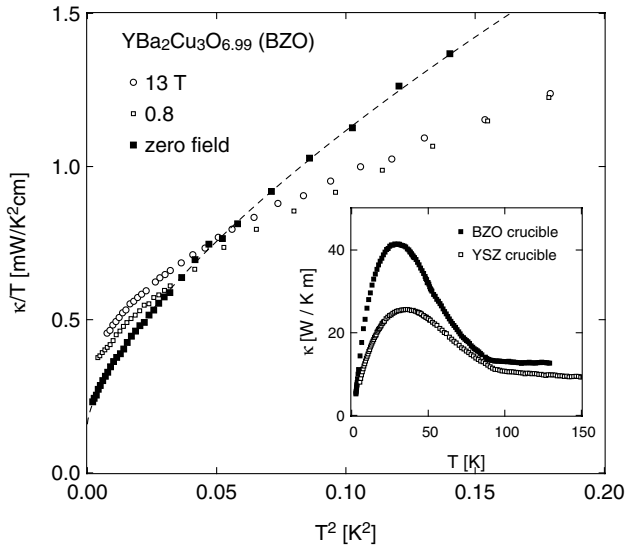


FIG. 1. Thermal conductivity divided by temperature versus T^2 for a high-purity YBCO sample for magnetic fields applied perpendicular to the ab plane. The dashed line is a guide to the eye. Inset: High-temperature data for YBCO samples grown in different crucibles.

κ/T to $T \rightarrow 0$, is entirely electronic. The question is how to extract any T dependence of κ_e/T . We use a magnetic field to do this. First, note that the zero-field curve in Fig. 1 shows a more rapid increase with temperature than the two in-field curves which are approximately parallel. On the assumption that the phonon transport at very low temperatures is limited by scattering from the boundaries of the sample (see [12]) and is unaffected by scattering from vortices, we can attribute this difference only to electrons. Furthermore, since all subsequent in-field curves lie parallel we assume that this additional electronic conduction is completely suppressed when a magnetic field is applied (see inset in Fig. 2), and the remaining temperature dependence of κ/T is due entirely to phonons. In other words, κ_{ph} is the T -dependent part of the 13 T data: $\kappa_{ph}/T = \kappa(13\text{ T})/T - \kappa_0(13\text{ T})/T$, where $\kappa_0(13\text{ T})/T = 0.31\text{ mW/K}^2\text{ cm}$. The electronic conductivity, κ_e/T , is then given by subtracting this from the total conductivity: $\kappa_e(H, T)/T = \kappa(H, T)/T - \kappa_{ph}/T$. This is shown in Fig. 2 for applied magnetic fields from 0–13 T.

The zero-field electronic conductivity shows a rapid growth with temperature, increasing by a factor of 5 within 0.5 K. The inset plots the same data on a T^2 temperature scale showing that the growth is cubic in temperature. As soon as a magnetic field is applied, this temperature dependence is completely suppressed (see inset in Fig. 2), an effect which can be attributed only to the scattering of quasiparticles by vortices. The possibility that the change in temperature dependence between zero and applied field is due to scattering of phonons by vortices is ruled out by the lack of field dependence above 0.8 T. By increasing the field to 13 T, an order of magnitude more vortices have been introduced

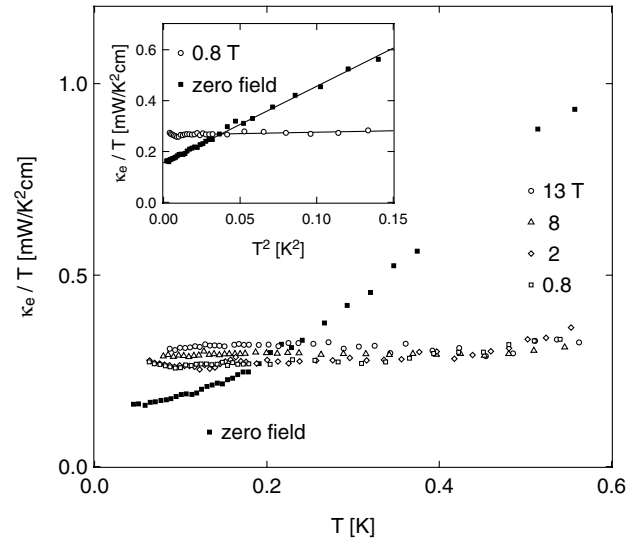


FIG. 2. Electronic thermal conductivity, plotted as κ_e/T vs T , for magnetic fields from zero to 13 T. The electronic contribution is extracted as discussed in the main text. Inset: The low field curves plotted against T^2 .

to the system, yet the total conductivity remains essentially unchanged.

Zero magnetic field ($H = 0$).—Using a self-consistent quasiclassical theory, formulated at low temperatures where heat transport is limited by electron scattering from random defects [13,14], the thermal conductivity due to quasiparticles at the nodes of a d -wave superconductor is given by [5]

$$\frac{\kappa_e}{T}(T) = \frac{\kappa_{00}}{T} \left[1 + \frac{7\pi^2}{15} \left(\frac{a^2 T}{\gamma} \right)^2 \right], \quad (1)$$

where κ_{00}/T is the universal conductivity limit, γ is the impurity bandwidth, and the coefficient a is strongly dependent on the scattering phase shift. This expression is valid in the dirty limit where $k_B T < \gamma$. The temperature dependence of our extracted electronic conductivity is well described by this form. Fitting this expression to the zero-field data (see inset in Fig. 2) gives $\kappa_e/T = 0.16(1 + 19.2T^2)$. Note that this corresponds to a huge 20-fold increase in κ_e/T by 1 K.

$H = 0$: Zero temperature.—The residual linear term, $\kappa_{00}/T = 0.16\text{ mW/K}^2\text{ cm}$, is in excellent agreement with the value published for optimally doped YBCO ($0.14\text{ mW/K}^2\text{ cm}$ [2]). This is direct confirmation of the universal nature of low temperature quasiparticle thermal conductivity. In this case we have measured a sample in the more difficult regime of increased purity, where we observe an order of magnitude lower scattering rate than previously and still recover the universal limit. (A slight increase in κ_{00}/T is expected based on the small increase in doping from $x = 6.95$ to $x = 6.99$ [12].)

$H = 0$: Finite temperature.—From the temperature dependent part of our fitted data we can estimate the impurity bandwidth and scattering rate. For scattering in the unitary limit $a = 1/2$ and the impurity bandwidth

γ is related to the normal-state scattering rate Γ_n by the relation $\gamma = 0.63\sqrt{\Delta_0\Gamma_n}$ [14]. Using the value from the fitted zero-field data (inset in Fig. 2), we obtain $\gamma \sim 0.25$ K and using $\Delta_0 = 2.14k_B T_c$, we get $\Gamma_n/T_c \sim 10^{-5}$; therefore, $\Gamma_n \sim 1 \times 10^8$ s $^{-1}$. Such a small scattering rate is unrealistic. Using $v_F = 2.5 \times 10^7$ cm/s [12], it would imply a normal-state mean free path as long as the longest dimension of the sample: $l \sim 1$ mm.

In the Born approximation, $a = (\pi v_2 \tau_0)/2$ and $\gamma = 4\Delta_0 \exp(-\pi\Delta_0/2\Gamma_n)$. Assuming a pure d -wave gap gives $v_2 = 2\Delta_0/\hbar k_F$ and using $\tau_0 = 1/2\Gamma_n$ leads to $\gamma \sim 3$ K and $\Gamma_n \sim 0.6\Delta_0 \sim 2.5 \times 10^{12}$ s $^{-1}$. Again we estimate a scattering rate that is unrealistic, in this case much too large. If the scattering rate were truly this magnitude it would lead to a substantial suppression of T_c , as noted previously [14], which is not observed experimentally.

From the measured temperature dependence of the electronic thermal conductivity, we conclude that the usual quasiclassical calculation cannot be correct if it treats impurity scattering with a single isotropic phase shift of either 0 (Born) or $\pi/2$ (unitary).

In a broader context, similar measurements on unconventional superconductors UPT $_3$ [15] and Sr $_2$ RuO $_4$ [4] reveal conductivities far too small to consider Born scattering. They are therefore analyzed in the unitary limit. Consistent with the present work, the trend that emerges is that a quantitative analysis of transport in the superconducting state, using the unitary limit, leads to mean free paths considerably longer than are consistent with normal-state measurements such as de Haas—van Alphen studies or resistivity above H_{c2} . This suggests that the standard theoretical approach to transport in unconventional superconductors is generically inadequate.

Microwave conductivity measurements [16,17] on samples of identical quality to that used in this study have also been compared to current theories of transport in unconventional superconductors [18]. These measurements reflect some but not all of the characteristics of weak scattering (Born limit) and point to either inadequacies in the conventional theories or the need to consider intermediate phase shifts, or both.

An earlier study on Bi-2212 reported an electronic conductivity, κ_e/T , that increased as T rather than T^2 [3]. The phonon contribution is subtracted by comparing measurements before and after electron irradiation. A linear T dependence is expected in the clean limit, where $\gamma < k_B T$. It is unclear, however, why Bi-2212 crystals with a level of disorder 2 orders of magnitude larger than our BZO-grown YBCO crystals should be in that limit. Indeed, it is a surprise that any T dependence of κ_e/T can be resolved in such crystals. (A 2-fold increase is observed by 1 K.)

Finite magnetic field ($H > 0$).—In Fig. 3 the extrapolated linear thermal conductivity at $T \rightarrow 0$ is plotted as a function of magnetic field. The values are normalized by the zero-field value κ_0/T . Also plotted is the previous data for an optimally doped YBCO ($x = 6.95$) sample grown

in a YSZ crucible [19]. In contrast to the latter sample, the much purer one shows a rapid increase at fields below $H = 0.4$ T followed by a sudden change to a regime where its behavior is almost field independent. Concomitantly, the coefficient of the T^2 term, and consequently the quasiparticle lifetime, collapses (see inset in Fig. 2). We interpret this as an indication that quasiparticle-vortex scattering is strongly influencing the transport in this very clean material.

Current semiclassical treatments of the effect of magnetic field on the low temperature electronic thermal conductivity predict smooth sublinear increases to within logarithmic corrections [6,20]. This arises when quasiparticle energies are Doppler shifted by the superfluid flow around magnetic vortices. Earlier measurements, reproduced in Fig. 3, on YSZ-grown samples [19] are well described by such theories and have been viewed as additional evidence for d -wave symmetry of the superconducting gap. Clearly, the field dependence of the measurements reported here on a BZO-grown sample is of completely different character and cannot be described by available theories. To emphasize this, the dotted line in Fig. 3 is the best fit for the theory of Kübert and Hirschfeld [6] to the initial rise of the conductivity. Intriguingly, the scattering rate deduced from this fit is an order of magnitude smaller than for the YSZ sample in agreement with the relative change inferred from the rise in thermal conductivity below T_c . This suggests that the rapid growth at low fields, due to the low impurity

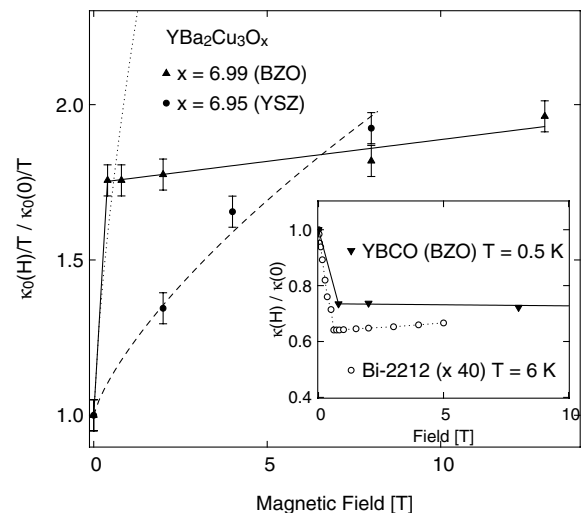


FIG. 3. Normalized residual electronic conductivity as a function of magnetic field for a slightly overdoped ($x = 6.99$), very pure, detwinned sample of YBCO (triangles). For comparison, the same is plotted for optimally doped YBCO ($x = 6.95$), where the sample is less pure [19], along with the fit to a semiclassical theory which describes the data [6] (dashed line). An attempt to fit the same theory to the BZO-grown sample is also shown (dotted line). Inset: High-temperature isotherm at 0.5 K for the pure sample compared to a magnified ($\times 40$) plot of an isotherm at 6 K for Bi-2212 [7].

scattering rate, is truncated by an additional scattering mechanism excluded from current theories.

A common feature of these theories is that at low temperatures the effect of scattering from vortices is expected to be negligible in comparison to impurity scattering. However, given the demonstrably low impurity scattering rate in this BZO-grown sample, we argue that such a simplification may be incorrect. Assuming these scattering mechanisms to be independent, one could add them in a Matthiessen-like manner. At zero field the conductivity will be in the impurity dominated regime, while in the very high-field limit, vortices will dominate the scattering. The crossover between these two limits will depend on the relative amount of impurity scattering and the cross section for vortex scattering. Such a model may also account for the similar magnitude of the conductivity at high fields for the two samples shown in Fig. 3, despite their obviously different impurity concentrations.

A similar strategy was adopted by Franz [21] to include scattering from a random vortex lattice. In this case the theory was developed to explain a plateauing of the field dependence of the thermal conductivity at higher temperatures and has yet to be extended to low enough temperatures for comparison with the data here. Nevertheless, the phenomenology may be correct; a \sqrt{H} increase coming from a Doppler shift is exactly compensated by scattering from vortices, where the scattering length is given by the intervortex separation $\sim\sqrt{H}$. What remains unusual is the sharpness with which this compensation turns on.

With this in mind, the inset in Fig. 3 shows the field dependence of an isotherm at 0.5 K. The behavior is reminiscent of earlier measurements on Bi-2212 [7], also shown as an isotherm at 6 K, where the high-field plateau is preceded by a “kink.” Such similarity, measured here for the first time in YBCO, is suggestive of a common origin. Since the present work is on a sample of the highest purity and in field-cooled measurements, this phenomenon cannot simply be dismissed as material dependent extrinsic behavior nor solely related to gap anisotropy [22]. The hysteresis seen in Bi-2212 measurements [8] is also naturally explained by the dominance of vortex scattering. The dramatic difference in magnitude between these two measurements is likely a consequence of the small electronic conductivity relative to the phonon contribution (which has not been subtracted) at 6 K in Bi-2212 and the comparatively huge electronic contribution measured in this high-purity YBCO.

An alternative explanation has recently been offered by Franz and Vafeek [23]. In their fully quantum-mechanical theory, the Meissner state (at zero field) and the vortex state emerge as two distinct d -wave states with different quasiparticle effective velocities. They both exhibit universal conductivity, with different values of the universal limit (see Fig. 2). This appealingly accounts for the fact that the conductivity of the two different YBCO samples

is the same not only at zero field but also at high fields (see Fig. 3). It is not clear, however, why the finite temperature correction to this universal limit should be so dramatically different in the two states.

In conclusion, when analyzed in terms of the quasi-classical theory of transport for a d -wave superconductor, the thermal conductivity of an extremely pure sample of YBCO reveals two features: (i) the universal limit as $T \rightarrow 0$ is confirmed and (ii) the usual assumption that impurity scattering can be treated as a single isotropic phase shift in the unitary limit (or the Born limit) is incorrect. Transport theory as it stands must be revised, at least in the clean limit, perhaps by going to intermediate phase shifts and maybe in more profound ways. Moreover, in the presence of a magnetic field, we find that transport appears to be rapidly dominated by vortex scattering, which can therefore not be neglected as it usually is.

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