Bulk Evidence for Single-Gap s-Wave Superconductivity in the Intercalated Graphite Superconductor C_6Yb

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We report measurements of the in-plane electrical resistivity ρ and thermal conductivity κ of the intercalated graphite superconductor C_6Yb down to temperatures as low as $T_c/100$. When a field is applied along the c axis, the residual electronic linear term κ_0/T evolves in an exponential manner for $H_{c1} < H < H_{c2}/2$. This activated behavior is compelling evidence for an s-wave order parameter, and is a strong argument against the possible existence of multigap superconductivity.

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Carbon is a remarkably versatile element—in its pure form it may exist as an electronic insulator, semiconductor, or semimetal depending on its bonding arrangement. When dopant atoms are introduced, superconductivity may be added to this list, observed in graphite [1,2], fullerenes [3], and even diamond [4]. Superconductivity in doped carbon was first discovered in the graphite intercalate compounds (GICs), materials composed of sheets of carbon separated by layers of intercalant atoms. The first of these compounds contained alkali atoms, and had modest transition temperatures of 0.13–0.5 K [1]. The recent discovery of T_c's two orders of magnitude higher than this in C_6Yb [5] and C_6Ca [5,6] has, however, refocused attention on this intriguing family of compounds.

The effects of the intercalant atoms in the GICs are twofold: they dramatically change the electronic properties of the host graphite lattice by both increasing the separation of the carbon sheets, as well as contributing charge carriers. This causes the two-dimensional graphite π^* bands to dip below the Fermi level. The graphite interlayer band, previously unoccupied, also crosses the new Fermi level, contributing three-dimensional, free-electron-like states located between the carbon sheets. This new interlayer band hybridizes strongly with the π^* bands, and its occupation appears to be linked with the occurrence of superconductivity in the GICs [7].

There are still several fundamental questions remaining about superconductivity in the GICs, especially in C_6Yb and C_6Ca, where little experimental data exist. The pairing mechanism is unresolved, with speculation ranging from a conventional route involving the intercalant phonons [8–10] to superconductivity via acoustic plasmons [7].

Early theoretical studies motivated by the alkali-metal GICs [11,12] emphasized a two-gap model for the superconducting state, where gaps of different magnitudes exist on different sheets of the Fermi surface. Such a scenario is plausible, as there are notable similarities between the GICs and MgB_2 [7,13], a known multigap superconductor. Indeed, some aspects of graphite intercalate superconductivity can be understood by this two-gap phenomenology; however, there is little direct evidence to support this picture, and recent band structure calculations suggest this scenario is unlikely [14].

A necessary starting point is to establish the superconducting order parameter, but in C_6Yb, this task is complicated as the intercalation procedure typically yields samples which are not fully intercalated. In addition, both C_6Yb and C_6Ca are very sensitive to air, and their surfaces rapidly deteriorate if left exposed. A recent study of penetration depth [15] on C_6Ca suggests that the superconductivity is s-wave; however, this technique is extremely surface sensitive, and the results were dependent on surface treatment. With these considerations in mind, we turn to measurements of bulk thermodynamic properties to probe the superconducting state.

The technique of thermal conductivity is ideally suited to the study of these materials. It is sensitive only to delocalized states, and in highly conductive systems such as C_6Yb the majority of the heat transport at low temperatures is provided by electrons, allowing us to easily separate out electronic and phononic contributions to the heat current. Most importantly, thermal conductivity is a *bulk* probe, only marginally affected by small concentrations of impurity phases.

In this Letter we report measurements of low-temperature thermal conductivity (κ) in C_6Yb, which we use to establish the nature of the superconducting order parameter in this compound for the first time. The behavior of κ as the superconducting state is suppressed with a magnetic field shows an activated dependence, clear evidence of s-wave superconductivity, and highly suggestive of a single-gap energy scale.

Thermal transport was measured down to 60 mK in a dilution refrigerator using a one heater, two thermometer steady state technique. Magnetic fields from 0 to 1 T were applied parallel to the c axis and perpendicular to the in-plane heat current. For measurements of $\kappa(T)$ at constant field, the sample was cooled in field from $T > T_c$ to maximize homogeneity of the vortex lattice.

Our samples were prepared by intercalating very pure highly oriented pyrolytic graphite (HOPG) using the vapor transport process described elsewhere [5]. In order to obtain samples consisting mainly of intercalated material, we first cleaved the graphite along the ab plane, and then took thin bars from the sides. The resulting samples were rectangular platelets of dimensions approximately 1 mm $\times$ 0.5 mm $\times$ 100 μm. Good quality electrical contacts were made using silver paint applied directly on the surface after cleaving, with all handling and mounting done in a glove box under flowing He.

Figure 1 shows the in-plane resistivity of C_6Yb as a function of field applied along the c axis. The residual resistivity ρ_0 is observed to be 4.5 $\mu\Omega$ cm by extrapolating the zero field curve, corresponding to a residual resistivity ratio of 16. The magnetoresistance (MR) is comparatively weak in C_6Yb, only 15% by 0.1 T at 6 K, compared to a factor of 80 increase at the same field in pure graphite at $T = 5$ K [16]. From the magnitude of ρ_0, we estimate the electronic mean-free path to be 1000 Å at low temperatures in zero field, assuming $k_F = 0.5$ Å^{-1} [11].

Figure 2 shows κ/T versus T for $H \parallel c$ axis. The fact that κ/T is almost constant reflects a dominant electronic contribution, since $\kappa_{\mathrm{electron}} \propto T$. Phonons, which are expected to contribute a thermal conductivity $\kappa_{\mathrm{phonon}} \propto T^3$ at low temperatures, are likely responsible for the small slope. By 1 T the sample is fully in the normal state, and a comparison to the electrical resistivity via the Wiedemann-Franz law is shown by the dashed line. In the normal state we see that this law is obeyed to within 5%, as expected for a metal in the elastic scattering regime, which gives us added confidence in our data.

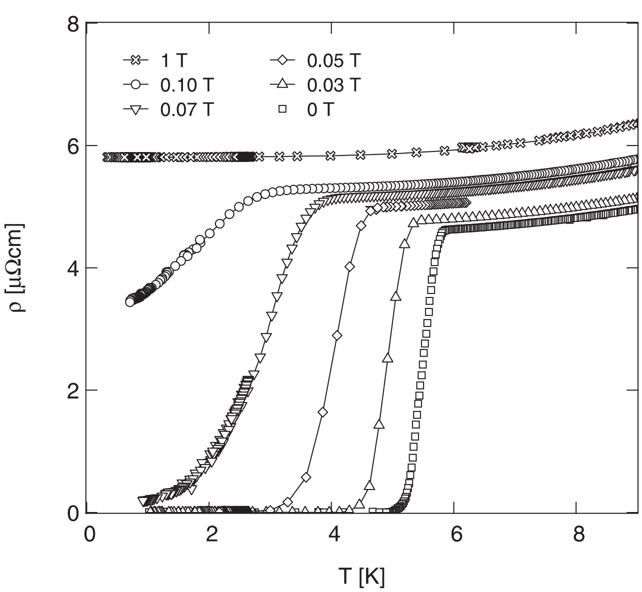

FIG. 1. In-plane resistivity for C_6Yb with $H \parallel c$. For $H = 0$ T the superconducting transition is sharp with $T_c = 5.4 \pm 0.4$ K but broadens with applied field. For $H = 1$ T superconductivity is entirely suppressed, revealing a metallic normal state with a residual resistivity $\rho_0 = 5.8$ $\mu\Omega$ cm. The strong positive magnetoresistance seen above T_c comes from small regions of pure, unintercalated graphite.

To analyze the electronic contribution to κ, we extrapolate our data to $T = 0$, where the residual linear term κ_0/T is unambiguously due to electrons. For the $H = 0$ data in Fig. 2 this yields a small but finite linear term, $\kappa_0/T \simeq 0.3$ mW K^{-2} cm^{-1}. It is tempting to attribute this as arising from nodal quasiparticles in the superconducting state [17,18], as observed, for example, in d-wave superconductors such as the high-T_c cuprates, where $\kappa_0/T = 1.41$ mW K^{-2} cm^{-1} for overdoped Tl-2201 with $T_c = 15$ K [19]. We can, however, rule out such an interpretation using two straightforward arguments.

First, we can estimate the magnitude of the expected linear term if the order parameter was unconventional. In a nodal superconductor, the size of κ_0/T is determined by the ratio of the quasiparticle velocities parallel (v_2) and perpendicular (v_F) to the Fermi surface near the nodes [18]. In a 2D d-wave superconductor with a gap maximum Δ_0 and a density of n planes per unit cell of height c we may write:

$$\frac{\kappa_0}{T} = \frac{k_B^2}{6} \frac{n}{c} k_F \left(\frac{v_F}{\Delta_0}\right) \tag{1}$$

assuming $v_F \gg v_2$. Using an average $v_F \simeq 3.4 \times 10^7$ cm/s [12], $k_F \sim 0.5$ Å^{-1} [11] and $\Delta_0 = 2.14 k_B T_c = 1.2$ meV we would expect $\kappa_0/T = 6.1$ mW K^{-2} cm^{-1} for this system. This is over an order of magnitude larger than what we measure. Second, pure graphite is characterized by an extremely strong magnetoresistance, which arises

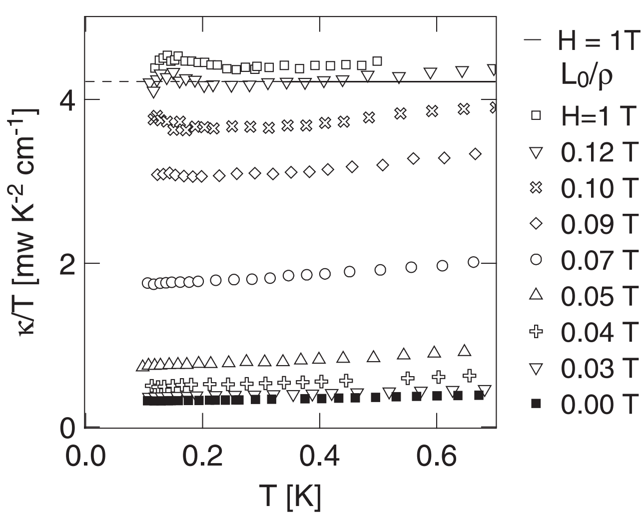

FIG. 2. Low-temperature thermal conductivity of C_6Yb as a function of applied field, with $\mathbf{J} \parallel ab$ and $H \parallel c$. The black line is the normal state Wiedemann-Franz law expectation estimated from the resistivity in $H = 1$ T.

from the fact that it undergoes a field-tuned metal-insulator-like transition. At a field of only 0.15 T along the c axis, for instance, the in-plane resistivity of graphite has been observed to increase 100-fold at low temperatures [16], whereas for a good metal like C_6Yb, we would expect a negligible MR in comparable fields. The observation of a 10% positive MR in the normal state of our sample, at a field of only 0.1 T and at temperatures well above T_c and away from the paraconductivity regime, is therefore almost certainly due to a small amount of graphite, at the 10% or so volume level. Having some 10% of unintercalated graphite in the sample will necessarily lead to a residual conduction of heat when the bulk of the sample has become superconducting, leading to a residual linear term that is roughly 10% of the normal state. In Fig. 2, the value of κ_0/T ($H = 0$) is seen to be $\sim$7% of the value of κ_0/T ($H > H_{c2}$), as expected. A measurement on a second sample confirmed precisely this correlation: it exhibited both a larger MR and a larger residual linear term. We therefore interpret the finite κ_0/T in zero field as arising from inclusions of pure graphite where full intercalation was not successful, and not from nodal quasiparticles.

We now turn to analyzing the field dependence of κ in C_6Yb. Figure 3 shows $\kappa/T(H)$ with T held constant at 300 mK. At these low temperatures, κ will be mainly due to electrons, as demonstrated by the small T^3 phonon contribution seen in Fig. 2. This is not surprising, as measurements in pure HOPG graphite show a phonon thermal conductivity of less than 10^{-2} mW K^{-2} cm^{-1} at 1 K [20], meaning that κ in Fig. 3 is essentially all due to electrons.

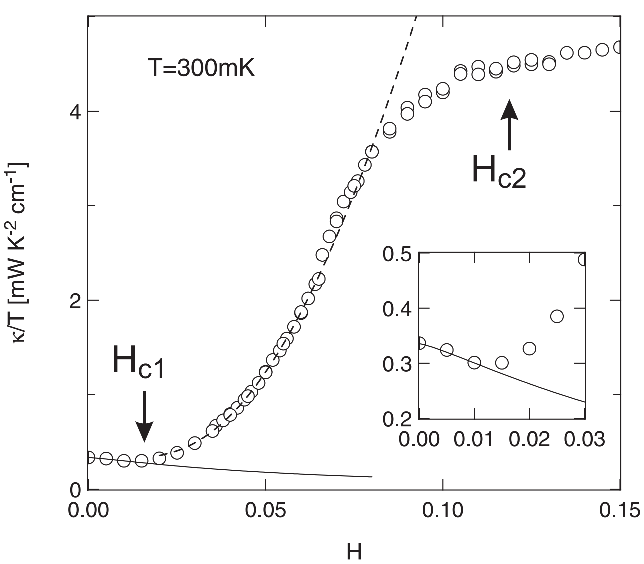

FIG. 3. (Main) Thermal conductivity of C_6Yb at $T = 300$ mK as a function of magnetic field, with H_{c1} and H_{c2} indicated. The dotted line is a fit to the behavior expected of an s-wave superconductor for $H_{c1} < H < H_{c2}/2$ [23]. The solid line is the contribution to the conductivity attributed to inclusions of pure graphite, characterized by positive magnetoresistance (see text). (Inset) Zoom at low fields.

Starting from $H = 0$ T, κ/T is seen to be very small, and decreases until $H \simeq 0.015$ T, as shown in the inset. This is consistent with the behavior of graphite inclusions. Using the fact that the MR of HOPG graphite was found to evolve as $H^{1.25}$ at low temperatures [21], we can extrapolate the expected conductivity due to these inclusions to higher fields and confirm that their contribution is negligible.

For fields higher than 0.015 T, a sudden increase in κ/T is observed, which we interpret as the onset of the vortex regime at $H > H_{c1}$. This agrees reasonably well with estimates of $H_{c1} = 0.04$ T at low temperatures from magnetization measurements [5].

As the field is further increased, the conductivity evolves in an exponential manner, precisely as expected for transport in the mixed state of an s-wave superconductor. As vortices first enter the sample at $H > H_{c1}$ the only quasiparticle states at $T \ll T_c$ are those associated within the vortex cores [22]. When the vortices are far apart, these states remain localized, and are unable to contribute to heat transport. Increasing the field decreases the intervortex spacing $d \sim \sqrt{\Phi_0/H}$ and the states begin to overlap, forming dispersive bands which yield a conductivity that grows exponentially with the ratio of the vortex spacing to the coherence length d/ξ, $\kappa \propto \sqrt{H} \exp(-\alpha\sqrt{H_{c2}/H})$, where α is a constant. This dependence is observed in simple s-wave superconductors such as Nb [23] for $H_{c1} < H < H_{c2}/2$, and is much different from that in nodal superconductors, where the conductivity is observed to increase as $\kappa \propto \sqrt{H/H_{c2}}$ [19]. A fit of our data to the simple s-wave form is shown in Fig. 3, and the good agreement forms the central result of our work: the evolution of the electronic conductivity is approximately exponential with applied field, providing the first verification of s-wave superconductivity in C_6Yb using a bulk thermodynamic technique.

At still higher fields, the conductivity rolls off and eventually saturates as the sample enters the normal state. From the data in Fig. 3 we estimate this to occur at $H \simeq 0.12$ T, in good agreement with estimates of $H_{c2} = 0.11$ T from magnetization measurements [5]. With $H_{c2}(\parallel c) = 0.12$ T we estimate $\xi_{ab} \simeq 525$ Å $\sim \ell_e$, which places C_6Yb in the dirty limit. This observation is consistent with the fact that the rise in conductivity with field is not as dramatic as in clean Nb [24], but closely resembles that observed in dirty limit Nb [25] and metal alloy superconductors [26].

In addition to confirming s-wave superconductivity, the activated behavior observed in Fig. 3 makes the multigap superconductivity scenario originally proposed for the GIC's [11] unlikely. In Fig. 4 we compare C_6Yb to other type-II superconductors by plotting the normalized value of κ_0/T versus applied field. The similarity between C_6Yb and the alloyed superconductor InBi with $T_c = 4.0$ K and $H_{c2} = 0.07$ T [26] is striking. Both curves are exponential with field at low H, crossing over to a roughly linear behavior closer to H_{c2} as expected for s-wave supercon-

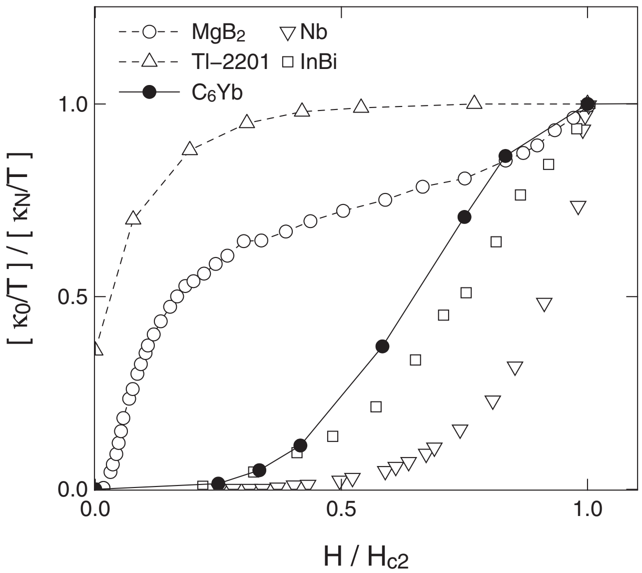

FIG. 4. Normalized residual linear term κ_0/T of C_6Yb plotted as a function of H/H_{c2}, with the small contribution from graphite impurities subtracted off. For comparison we also display low-temperature data for the clean s-wave superconductor Nb [24], the dirty s-wave superconducting alloy InBi [26], the multigap superconductor MgB_2 [28], and an overdoped sample of the d-wave superconductor Tl-2201 [19].

ductors in the dirty limit [27]. The clean limit case observed in pure Nb [24] is shown for contrast. These three curves are very different from the behavior of the archetypal multiband superconductor MgB_2 [28], or the well-known d-wave superconductor Tl-2201 [19].

In the multiband superconductivity scenario [11], gaps of different magnitudes are associated with distinct π and σ bands. Such a situation is expected when electron-phonon coupling differs for each band, or when coupling with one band induces superconductivity in another [29]. Applying a field rapidly delocalizes quasiparticles states confined within the vortices associated with the smaller gap band, while those states associated with the larger gap band delocalize more slowly. This gives rise to the rapid increase in conductivity at low fields and relatively flat dependence at higher fields [30], evident, for instance, in the MgB_2 [28] data shown in Fig. 4. This behavior is most apparent when both bands contribute equally to transport, for example, when the density of states, scattering rates, and Fermi velocities associated with each band are comparable. Calculations for C_8K [11,12] suggest that this should indeed be the case for the graphite intercalates, so the lack of a distinctive "elbow" in the field dependence of the thermal conductivity should be taken as support for a single-gap energy scale for the electrons in C_6Yb.

In summary, we have used bulk measurements of thermal conductivity to provide strong evidence of s-wave superconductivity in C_6Yb, and rule out an order parameter with nodes. The activated behavior of κ_0/T also strongly suggests that the pairing state is isotropic, with a gap of roughly equal magnitude on all Fermi surface sheets, as in elementary type-II superconductors in the dirty limit. It will be interesting to confirm these results on other members of the intercalate family with complementary techniques, although it seems likely that other GICs will share similar superconducting properties.

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