Specific heat of $Bi_2Sr_2CuO_6$ and $Bi_2Sr_2CaCu_2O_8$ in the superconducting state

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We have measured the specific heat $C(T)$ of single-phase samples of the cuprate superconductors $Bi_2Sr_2CuO_{6-\delta}$ (2:2:0:1; $T_c=12.5$ K) and $Bi_2Sr_2CaCu_2O_{8-\delta}$ (2:2:1:2; $T_c=84$ K) in the temperature range 3–11 K. Bulk superconductivity with a Meissner fraction of about 25% is observed for both materials. We find no strong evidence for a term in $C(T)$ linear in the temperature T; rather, $C(T)/T$ is a linear function of T^2 in this temperature range. A least-squares fit gives an upper bound of 0.35 mJ/Cu K^2 for any linear term. This result appears to rule out gapless pairing and gap functions with lines of nodes in these materials. Though gap functions with point nodes are not excluded by our results, we demonstrate that possibility to be unlikely in these materials. We suggest further experiments to test whether such T^3 electronic contribution to the specific heat exists for the 2:2:0:1 material.

INTRODUCTION

There has been considerable experimental and theoretical interest in the low-temperature specific heat of the new cuprate superconductors. Experimental interest arose from the observation of linear terms in both superconducting polycrystalline $La_{2-x}Ba_xCuO_{4-\delta}$ and superconducting (polycrystalline and single crystal) $YBa_2Cu_3O_{7-\delta}$,[1,2] which are of the usual magnitudes for a metal (several mJ/mole K^2). These results were initially considered consistent with the interesting theoretical possibility of low-lying neutral fermionic excitations, which may be found, for example, in a resonating-valence-bond (RVB) based superconducting state.[3] However, subsequent theoretical considerations have shown that the RVB states can give, at best, a T^2 coefficient in the specific heat.[4]

The likely cause of this linear term has been pointed out.[5] $BaCuO_2$ is the most common impurity phase which forms during preparation of $YBa_2Cu_3O_{7-\delta}$, and for unknown reasons this material has an enormous low-temperature linear specific heat (of the order of hundreds of mJ/mole K^2). The presence of a few percent of this impurity phase could easily give rise to the observed linear specific heat.

It would be of interest therefore to examine cuprate superconductors[6] which contain no barium. Fortunately, the discovery of the bismuth-based superconductors $Bi_2Sr_2CuO_6$ (2:2:0:1) (Refs. 6 and 7) and $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2) (Refs. 8–12) afford such an opportunity. Observation of a linear term in these materials would lend support to the notion that it is an intrinsic property of the cuprate materials, while its absence clearly points to $BaCuO_2$ as its source in the other materials.

We have performed low-temperature specific-heat measurements on $Bi_2Sr_2CuO_{6-\delta}$ [2:2:0:1 ($T_c=12.5$ K) (Ref. 6)] and $Bi_2Sr_2CaCu_2O_{8-\delta}$ [2:2:1:2 ($T_c=84$ K) (Ref. 10)] materials. In agreement with results obtained elsewhere,[13] we have detected no strong evidence for a linear term in the specific heat. We demonstrate below that our data appear to rule out gapless pairing and gap functions with nodal lines for the superconducting oxygen holes in these materials. Moreover, we show that pair states possessing gaps with point nodes are highly unlikely.

Our paper is organized as follows: First, we discuss the materials preparation and experimental techniques, then we present the data, and finally we shall discuss the implications for theory presented by our data.

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Samples of 2:2:0:1 $Bi_2Sr_2CuO_{6-\delta}$ and 2:2:1:2 $Bi_2Sr_2CaCu_2O_{8-\delta}$ were prepared by the standard solid-state reaction technique.[14] Stoichiometric quantities of Bi_2O_3, SrO_2, Ca_2CO_3, and CuO were ground together, placed in gold crucibles, and fired in air. The 2:2:0:1 sample was heated to 950 °C (above the melting point), slow cooled at 10 K per hour to 700 °C, and then furnace cooled. Large single crystals of 2:2:0:1 formed, the micaceous nature of which is reflected in the strong (001) preferred orientation seen in the powder pattern. In contrast, 2:2:1:2 samples were fired at 850 °C (below the melting point) in order to avoid incongruent melting (formation of 2:2:0:1). The 2:2:1:2 samples were reground and refired three times. The x-ray-diffraction pattern measured in a Scintag diffractometer showed the samples to be single phase within the sensitivity of that method (1%–3%).

The superconducting transition temperature was determined by magnetization measurements. We find for our 2:2:0:1 sample $T_c=12.5$ K, while for our 2:2:1:2 sample, $T_c=84$ K. In each case, Meissner exclusion was 26% of the ideal value.

The specific-heat measurements were performed in an

adiabatic calorimeter using a drift technique.[15] The sample is weakly coupled to the temperature reservoir via a copper link (typically 2-mil Cu wire, approximately 20 cm long, wound in the form of a spiral). One can measure specific heat reliably up to about 10 K, making use of the fact that the thermal conductivity of copper is essentially linear in temperature to 10 K. The samples were pellet form with mass of order 1–2 g. For use as thermometers 220-Ω Allen-Bradley resistors were ground to a mass of 15 mg and then mounted on the samples. They were calibrated *in situ* against a carbon-glass thermometer mounted on the temperature reservoir. The heater wire wound around the sample pellet weighed only a few milligrams. The contribution of sample peripherals was therefore kept to within a few percent of the sample by weight, and their contribution could be reliably subtracted.

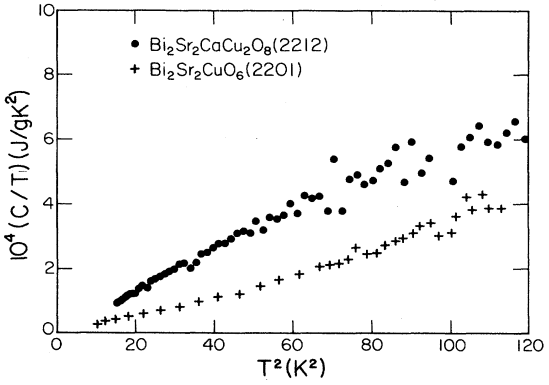

FIG. 2. Specific heat C/T vs T^2 for $Bi_2Sr_2CuO_6$ and $Bi_2Sr_2CaCu_2O_8$.

RESULTS FOR THE SPECIFIC HEAT

Figure 1 displays $C(T)$ vs T for our samples. In the temperature range shown, both samples are in the superconducting state. The data are replotted in Fig. 2 as $C(T)/T$ vs T^2. The absence of a finite intercept in Fig. 2 confirms the absence of a linear term in the specific heat. A least-squares fit of $C(T)/T$ vs T^2 below 7.5 K gives an upper limit on the linear term in the specific heat to be of the order of 0.3 and 0.35 mJ/Cu K^2 for the 2:2:1:2 and 2:2:0:1 samples, respectively. The linearity in T^2 is consistent with a simple Debye form, and with this assumption we obtain Debye temperatures of 212 K (2:2:0:1) and 171 K (2:2:1:2). These values are comparable to those obtained elsewhere for other cuprate superconductors[16] and change as expected as more atoms are added to the unit cell.

IMPLICATIONS

It is immediately clear that our data do not rule out an activated contribution to $C(T)$ which arises from a uniform gap as found in conventional superconductors or the Balian-Werthamer[17] triplet state. The data strongly constrain the form of possible power-law contributions from other superconducting states, which we shall discuss in turn below.

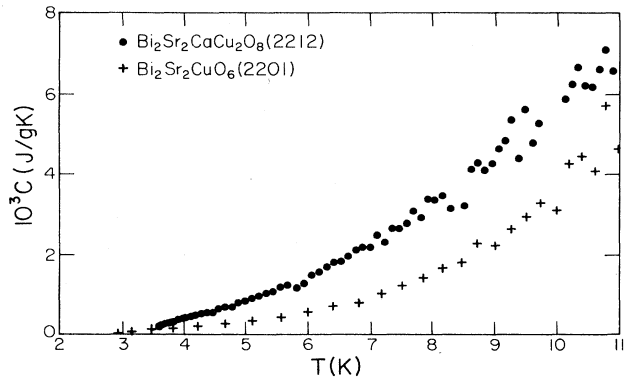

FIG. 1. Specific heat vs T for $Bi_2Sr_2CuO_6$ and $Bi_2Sr_2CaCu_2O_8$.

States with lines of nodes. Our data rule out pairing corresponding to a gap function with lines of nodes on the Fermi surface, since this would generate a linear in T contribution to $C(T)/T$, which would produce a negative curvature not evident in our data.

Gapless pairing. Though not as exclusively, our results appear to rule out gapless pairing[18] for these materials arising from disorder-induced filling in of a uniform gap in the quasiparticle density of states. The reason is that this would lead to an anomalously small specific-heat jump at T_c, which is not observed, at least in the 2:2:1:2 material.[19] The logic is as follows: gapless pairing would lead to a low-temperature linear contribution. We have an upper bound of 0.35 mJ/Cu K^2 for the linear coefficient in the superconducting state from our least-squares fit. Photoemission experiments suggest that the normal-state Fermi-level density of states is about 0.25–0.33 that of elemental copper,[20] so that we can assume a reference value of about 1 mJ/mol K^2. By utilizing the standard pair-breaking theory,[18] this translates to an 82% reduction of T_c from the value with no pair breaking, and thus about an order-of-magnitude reduction of the specific-heat jump, which is clearly not observed in the 2:2:1:2 material.[19]

Pairing with point nodes. A more interesting possibility is a gap function which has point nodes and which will therefore produce a T^2 contribution to $C(T)/T$. While we cannot prove that this possibility applies here, we can place a bound on the observability of such a specific-heat contribution by doing a rough order-of-magnitude estimate on a spherical Fermi surface.[21] For definiteness, assume we have an axial Anderson-Brinkman-Morel (ABM) type state such that the quasiparticle energy in the superconducting state has the form $E_{\mathbf{k}}=\{\epsilon_k^2+[\Delta\sin(\theta)]^2\}^{1/2}$ which clearly has point nodes. In weak-coupling theory, $\Delta=2.0k_BT_c$ with this normalization, and in the superconducting state the electrons contribute a T^3 specific heat per electron of

$$C_s(T)=\frac{7\pi^4}{15}k_B(k_BT)^3\frac{N(E_F)}{\Delta^2}, \quad (1)$$

where $N(E_F)$ is the Fermi-level density of states. Taking a free-electron form for the normal-state density of states, the ratio of $C_s(T)$ to the lattice contribution $C_l(T)$ per unit cell gives

$$R=\frac{C_s(T)}{C_l(T)}=\frac{7}{24}\left[\frac{k_B\Theta_D}{\Delta}\right]^2\frac{\Theta_D}{T_F}, \quad (2)$$

where $T_F=E_F/k_B$. Assuming $T_F=5000$ K (consistent with a low-carrier density of about 10^{21} carriers/cm^3), and using T_c and Θ_D from our measurements, we see that this ratio is about 1.8 for the 2:2:0:1 material and about 0.02 for the 2:2:1:2 material.

In surveying the group theoretically allowed superconducting states in tetragonal symmetry, it is clear that the only states possessing point nodes are spin-triplet axial-like pairing states with the symmetry axis oriented along the crystalline c axis.[22] These point nodes will only occur for a Fermi surface which is closed along the symmetry axis. Since in this layered material the effective mass along the c direction is presumed large, it is not clear whether the Fermi surface will close: for infinite effective mass along the c direction, we obtain an open, cylindrical Fermi surface.

We note that most[23,24] (but not all[25]) of the proposed pairing mechanisms for high-T_c materials favor singlet pairing. In conjunction with the above comments about the Fermi surface, we therefore consider it unlikely that the superconductivity in these materials is characterized by a gap function with nodes.

However, we can only rigorously say from our data that a T^3 electronic contribution to $C(T)$ arising from a gap function with point nodes, cannot be ruled out. For the 2:2:1:2 material, it is likely to be a small and difficult to observe contribution. For the 2:2:0:1 material, if it exists, it should be comparable to the lattice specific heat, since the lattice specific heat used above was obtained under the assumption that all the T^3 contribution to $C(T)$ arose from phonons.

The presence of such an electronic contribution to $C(T)$ in the 2:2:0:1 material may be tested by measuring the T^3 contribution to $C(T)$ for T greater than T_c. This is beyond the capability of our current experimental setup. If the T^2 coefficient of $C(T)/T$ above T_c is substantially reduced (by approximately 50%) relative to the T^2 coefficient of $C(T)/T$ for T much smaller than T_c (note that the electronic T^3 term is only asymptotically true for T much smaller than T_c), one would find strong evidence for an electronic T^3 contribution to $C(T)$. Alternatively one can attempt substitution of nickel for copper in the 2:2:0:1 samples and use that material as a bulk-lattice specific-heat reference; or else direct measurement of the phonon density of states by inelastic neutron scattering can be employed to reliably estimate the lattice contribution.

SUMMARY

We have performed measurements of the specific heat of the layered cuprate superconductors $Bi_2Sr_2CuO_{6-\delta}$ and $Bi_2Sr_2CaCu_2O_{8-\delta}$. In agreement with other groups, we find no linear term in the superconducting phase; instead, $C(T)$ is apparently proportional to T^3. Such a result is consistent with a normal Debye specific heat plus an electronic contribution arising from a superconducting gap function possessing point nodes, though we consider the latter contribution an unlikely one. The reason is that only triplet states can give point nodes in tetragonal symmetry, and they can only do so along the tetragonal c axis. The large effective mass along that direction makes the prospect of a closed oxygen hole Fermi surface unlikely. A hypothetical electronic contribution to the T^3 term in $C(T)$ would likely be small and undetectable for the 2:2:1:2 material; if present, it should contribute at an observable level for the 2:2:0:1 material. Assessment of this possibility in the 2:2:0:1 material can be made through measurement of $C(T)$ above T_c; or subtraction of the lattice contribution by complete nickel substitution for copper (if possible), or by measurement of the phonon density of states via neutron scattering.

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