Magnetic Field Dependence of the Density of States of $YBa_2Cu_3O_{6.95}$ as Determined from the Specific Heat

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The magnetic field dependence of the electronic density of states at the Fermi level, $N(E_F, H)$, is determined in single-crystal $YBa_2Cu_3O_{6.95}$ by specific heat measurements. The total specific heat is best described by including two predictions for the electronic specific heat of d-wave superconductivity: a T^2 term in zero field and an increased linear term in a magnetic field applied perpendicular to the CuO_2 planes. The additional linear term, which implies a finite $N(E_F, H)$, obeys $N(E_F, H) \propto (H/H_{c2})^{1/2}$ as predicted by Volovik for superconductivity with lines of nodes in the gap.

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Any theory of high-temperature superconductivity must be consistent with the specific heat, which is sensitive to *all* of the low-energy excitations in a system. A fully gapped superconductor will have an exponentially activated electronic specific heat, while a superconductor which is not fully gapped will have an electronic specific heat which rises as some power of the temperature. There are ongoing investigations of the possibility of $d_{x^2-y^2}$ symmetry in some of the high-T_c materials, particularly $YBa_2Cu_3O_{7-\delta}$ (YBCO) and $Bi_2Sr_2CaCu_2O_8$ [1]. Measurements on single-crystal $YBa_2Cu_3O_{6.95}$ by Hardy *et al.* show a linear temperature dependence of the penetration depth [2], as predicted for a clean d-wave superconducting state [3]. For such a state, the density of states rises linearly with energy at the Fermi level, which should result in an electronic specific heat which depends quadratically on the temperature [4–6]. However, such a term in the specific heat is difficult to identify in the presence of other, much larger, contributions.

The magnetic field dependence can help to distinguish different contributions to the specific heat. Volovik has recently calculated the magnetic field dependence of the density of states (DOS) at the Fermi level for a superconducting state with lines of nodes in the gap function, such as d-wave [7]. He predicts that the quasiparticle excitation spectrum is shifted by the superfluid velocity about the core, resulting in a density of states $N(E_F, H) = kN_n[H/H_{c2}]^{1/2}$, where N_n is the normal-state DOS and k is of order 1. The quasiparticles which contribute to this DOS come from the region far from the vortex cores in position space and close to the nodes in momentum space. By contrast, in a clean s-wave superconductor, the quasiparticles are confined to the vortex cores. For a short coherence length ($\xi_0 = 15$–17 Å in YBCO), the estimated quantum confinement energy is high [8,9], and there is no expected enhancement of the DOS from vortex-core contributions. Thus, a nonzero $N(E_F, H)$ in YBCO is difficult to explain without the existence of nodes in the gap.

In this paper we report measurements of the magnetic field dependence of the specific heat of a $YBa_2Cu_3O_{6.95}$ single crystal grown at the University of British Columbia [10]. The specific heat is compared for magnetic fields applied parallel and perpendicular to the a-b planes (Fig. 1). In perpendicular field, the coefficient of the linear term in the specific heat is increased by an amount $\gamma_\perp(H)$, indicating a field-dependent density of states $N(E_F, H)$. A global fit which includes the data at zero field and five nonzero perpendicular fields agrees with the predictions of d-wave superconductivity: a quadratic term in the zero-field specific heat and a magnetic field dependence of the linear term which is given by $\gamma_\perp(H) \propto [H/H_{c2}]^{1/2}$ (Fig. 2). To our knowledge, this work is the

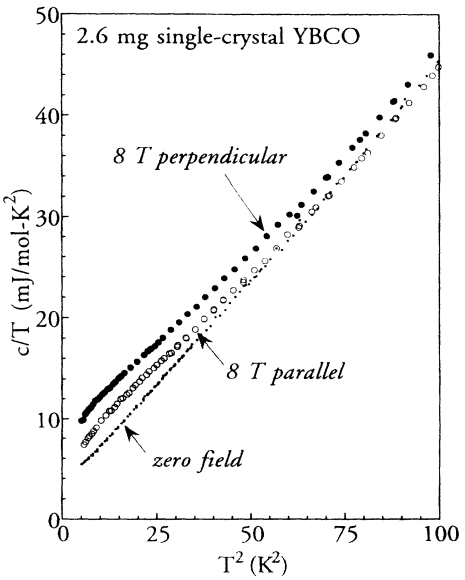

FIG. 1. The total specific heat, plotted as c/T vs T^2. The magnetic field is applied either parallel or perpendicular to the CuO_2 planes. The increased linear term in perpendicular field $\gamma_\perp(H)$ implies a field-dependent density of states $N(E_F, H)$.

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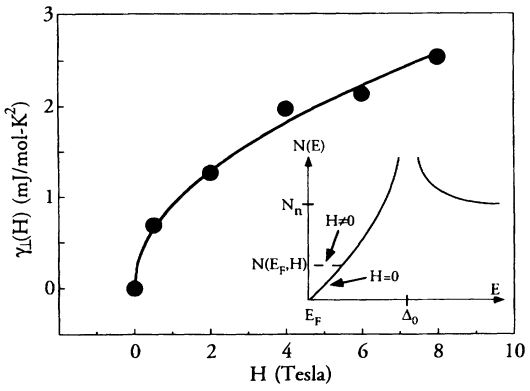

FIG. 2. The coefficient of the field-dependent linear term $\gamma_\perp(H)$ vs H. This solid line is a fit by $\gamma_\perp(H) = AH^{1/2}$ with $A = 0.91$ mJ/mol K^2 T$^{1/2}$, as predicted for lines of nodes. Inset: schematic of the density of states.

first investigation of the possibility of a nonlinear field dependence of $\gamma(H)$.

The data reported in this paper were taken on a 2.6 mg single crystal grown by the same flux-growth technique [10] as those crystals which show linear temperature dependence of the penetration depth [2]. The crystal had $T_c = 93$ K with a width of <0.4 K as determined by SQUID magnetometry. Optical and scanning electron microscopy showed the surface and edges of the crystal to be clean, with a few flux spots which occupied <0.1% of the sample volume. Microprobe analysis showed these flux spots to be $BaCuO_y$. After the measurements in a field were complete, the flux spots were scraped off the sample and the zero-field specific heat was found to be unchanged. The sample was then cut into pieces: no evidence of impurity inclusions was found.

The specific heat was measured using a relaxation method described in detail elsewhere [11]. The sample was mounted on a sapphire substrate with a weak thermal link (thermal conductance κ_w) to a constant-temperature copper block. κ_w was measured at each temperature and field by applying power $P = \kappa_w(T_{\text{sample}} - T_{\text{block}})$. A smaller temperature difference was then used to measure the total heat capacity C. When the power was turned off, the sample temperature relaxed exponentially to the block temperature with a time constant $\tau = C\kappa_w$. The precision of the measurement in the temperature range 2–10 K is ~0.5%, and the absolute accuracy is limited by the addenda (about half of the total heat capacity) to ~10%. Measurements of an empty substrate showed that the addenda heat capacity does not depend on the applied magnetic field within the precision of the data, so the accuracy of the field dependence of the specific heat is better than 1%.

The specific heat at 0 and 8 T is shown in Fig. 1. In zero field, the specific heat is predominantly composed of a linear term $\gamma(0)T$ and a Debye term βT^3. The phonon specific heat starts to deviate from T^3 above 8 K, and to avoid this complication, the data are only fitted below 7 K. In a magnetic field applied parallel to the planes, the specific heat is approximately the same as in zero field, with the addition of a Schottky anomaly from spin-$\frac{1}{2}$ magnetic impurities. The data in perpendicular field appear to have an additional linear term $\gamma_\perp(H)T$ such that the total linear term is $[\gamma(0) + \gamma_\perp(H)]T$, as well as Schottky contribution. Neither the lattice specific heat nor possible contributions from impurity inclusions should be anisotropic. Contributions from vortices or other electronic excitations would be highly anisotropic, and we interpret $\gamma_\perp(H)$ as an intrinsic electronic effect.

The size of the linear term in the zero-field specific heat is similar to that seen in previous measurements of YBCO: typical values of the linear term are $\gamma(0) \geq 4$ mJ/mol K^2 [12]. However, $\gamma(0)$ is correlated with various types of impurities [12,13], and the CuO chains may also contribute to $\gamma(0)$. We treat the zero-field linear term $\gamma(0)T$ in this sample as an additive contribution which is extrinsic to the superconductivity. This assumption leads to a self-consistent analysis of the field dependence of the specific heat.

The electronic specific heat of a fully gapped superconductor with a minimum gap Δ_{min} is exponentially activated as $\exp(-\Delta_{\text{min}}/k_BT)$, which is a negligible contribution for $k_BT \ll \Delta_{\text{min}}$. In contrast, the low-lying excitations in a superconductor with lines of nodes should contribute to the specific heat even at low temperatures. The d-wave density of states rises linearly with energy at the Fermi level, $N(E - E_F, H = 0) \propto E$ (Fig. 2, inset). The number of states accessible to thermal excitation rises as N_nT^2/T_c, while the average energy of these states rises as k_BT, so the total energy is proportional to $k_BN_nT^3/T_c$. This results in an electronic specific heat αT^2, where $\alpha \cong \gamma_n/T_c$, and γ_n is the coefficient of the linear term in the normal state. More detailed calculations of α have been done in Refs. [4–6]. Allowing for a quadratic term, the zero-field specific heat is described by

$$c(T) = \gamma(0)T + \alpha T^2 + \beta T^3. \quad (1)$$

Volovik predicts a finite density of states at the Fermi level $N(E_F,H)$ in a magnetic field (Fig. 2, inset). As a result, the zero-field αT^2 term should be replaced by a $\gamma(H)T$ term in a magnetic field in the low-temperature limit. The limiting temperature is roughly estimated as $T \approx T_cN(E_F,H)/N_n \approx T_c[H/H_{c2}]^{1/2}$. Taking $H_{c2} = 120$ T, the linear-T behavior should be valid below ~6 K for $H \geq 0.5$ T and below ~24 K for $H \geq 8$ T.

The specific heat was measured in perpendicular field at $H = 0.5$, 2.0, 4.0, 6.0, and 8.0 T. The magnetic field dependence includes an unchanged Debye term, an increased linear term, and a 2-level Schottky anomaly due to a small concentration of unpaired spin-$\frac{1}{2}$ magnetic moments. These data sets are described by

$$c(T,H) = [\gamma(0) + \gamma_\perp(H)]T + \beta T^3 + nc_{\text{Schottky}}(g\mu H/k_BT), \quad (2)$$

where

$$c_{\text{Schottky}}(x) = x^2 e^x/(1 + e^x)^2 . \quad (3)$$

Comparison of the data in parallel and perpendicular field shows ~10% anisotropy in the Lande g factor, with $g = 2.0$ for perpendicular field and larger g in parallel field [14]. This anisotropic g factor is in agreement with ESR data [15].

All six data sets are fitted simultaneously by Eqs. (1)–(3), without imposing any assumptions about the functional form of $\gamma_\perp(H)$. Thus, β and n are constrained by multiple data sets, $\gamma(0)$ and α are constrained by the zero-field data, and $\gamma_\perp(H)$ is allowed a different value at each field. This fit gives $\gamma(0) = 3.06$ mJ/mol K^2, $\alpha = 0.11$ mJ/mol K^3, $\beta = 0.392$ mJ/mol K^4 ($\theta_D = 400$ K), and $n = 24.0$ mJ/mol K (0.10% spin-$\frac{1}{2}$ impurities per Cu atom). Figure 3 shows the field-dependent components of the data sets, along with the fit. The total rms deviation of the data from the fit is 0.8%.

Predictions for the coefficient of the T^2 term α depend either on γ_n [4,5] or on the Fermi velocities [6]. Scalapino finds $\alpha = k'[3.28 k_B \gamma_n/\Delta]$, where Δ is the maximum gap [5]. The factor k' of order 1 is included because γ_n usually denotes a Fermi surface average of the DOS, while α is only sensitive to the DOS near the nodes. Published values of γ_n range from 9 to 40 mJ/mol K^2 [12]. The best values are determined by modeling the total specific heat near T_c [12] and by differential calorimetry [12,16], and these values are in the range 15–20 mJ/mol K^2. Taking the maximum gap to be $\Delta = 20$ meV gives $\alpha = k[(0.2–0.3)$ mJ/mol K^3], comparable to the $\alpha = 0.11$ mJ/mol K^3, which results from the fit.

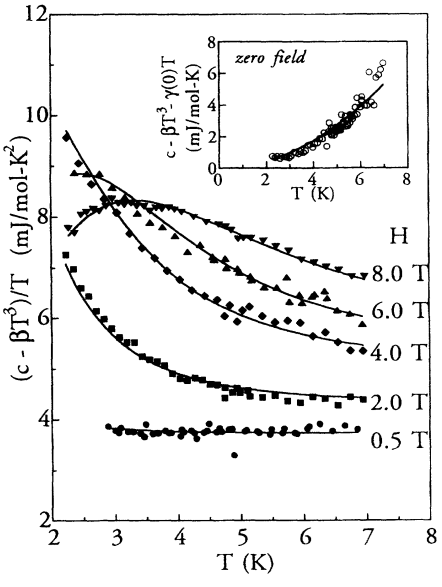

FIG. 3. The nonphonon specific heat, plotted as $(c - \beta T^3)/T$ vs T. The magnetic field is applied perpendicular to the plane. The solid lines are the linear and Schottky terms determined by the fit by Eqs. (1)–(3). Inset: zero-field electronic specific heat $c - \beta T^3 - \gamma(0)T$ vs T. The solid line is a fit by αT^2 with $\alpha = 0.11$ mJ/mol K^3.

The αT^2 term is ~5% of the total zero-field specific heat at 5 K, while the absolute accuracy of the data is ~10%. Thus, a small T^2 term cannot be reliably distinguished from a slightly larger Debye T^3 term in the zero-field data: fitting the zero-field data by Eq. (1) and requiring $\alpha = 0$ results in $\gamma(0) = 3.1$ mJ/mol K^2, and $\beta = 0.41$ mJ/mol K^4. The value of β resulting from fits of the individual data sets in nonzero field, where the T^2 term is suppressed, are significantly lower (ranging from 0.385 to 0.397 mJ/mol K^4). Since the relative accuracy between data in different fields is better than 1%, using a global fit to determine β allows a more accurate determination of the field-dependent parameters α and $\gamma_\perp(H)$.

The field-dependent linear term $\gamma_\perp(H)$ depends on the square root of the field as $\gamma_\perp(H) = AH^{1/2}$, with $A = 0.91$ mJ/mol K^2 T$^{1/2}$ (Fig. 2). This coefficient agrees with the prediction [4] $A = k\gamma_n/H_{c2}^{1/2}$ within the range of accepted values for γ_n and H_{c2}. An upper limit can be set on potential contributions to $\gamma(H)$ from $BaCuO_y$. $BaCuO_y$ has a zero-field linear term of about 100 mJ/mol$_{\text{BCO}}$ K^2 [12,13], so that at most 1% of the copper in this sample could be present in this form. According to measurements of the magnetic field dependence of the specific heat of $BaCuO_y$ [12], potential impurities in our sample could not contribute more than 5% of the measured $\gamma_\perp(8$ T).

Equations (1)–(3) provide a good description of the data compared to other models which we attempted to fit. Among other possibilities, we tried allowing the contribution of the magnetic moments to deviate from a perfect Schottky anomaly, excluding the T^2 term from the zero-field fit, allowing field dependence of θ_D, or explicitly imposing a linear dependence on $\gamma_\perp(H)$. Fits which did not explicitly assume a linear dependence of $\gamma_\perp(H)$ on H resulted in a weaker-than-linear dependence.

Interactions between the free spin-$\frac{1}{2}$ particles may alter the Schottky anomaly from Eq. (3). For example, other authors have fitted the low-field Schottky with a series expansion [17] or allowed n to vary as a function of field [18,19]. The limits on the Schottky contribution to our data at 0 and 0.5 T set an upper limit on the effective internal field of $H_{\text{int}} \leq 0.5$ T. Interactions would be most important at low and zero fields, and $\gamma(0)$ and $\gamma_\perp(0.5$ T) are not significantly changed by including an effective interaction field in Eq. (3).

We also compared the specific heat when the field was applied at 0° and 45° angles to the twin boundaries within the a-b plane. No anisotropic magnetic field dependence of the specific heat with the field applied parallel to the plane was found within the precision of the measurement. In fitting the parallel-field data by Eqs. (2) and (3), an increased linear term $\gamma_\parallel(H)$ is not necessary to describe the data, although a small $\gamma_\parallel(H)$ (<0.5 mJ/mol K^2) is allowed. This $\gamma_\parallel(H)$ is difficult to identify conclusively because of the possibility of a small sample misalignment.

The agreement of A and α with theory depends on published values of γ_n. Other comparisons can be made:

(1) γ_n can be eliminated by comparing A and α. Since k and k' correct γ_n for angle and energy dependence of the DOS in a similar way, we expect $k \approx k'$. The assumption $k = k'$ gives $H_{c2} \approx [\alpha T_c/A]^2 = 115$ T or $H_{c2} \approx [\alpha\Delta/3.28k_BA]^2 = 73$ T, corresponding to $\xi_0 = 17$ and 21 Å, respectively.

(2) As discussed above, taking $\gamma_n = 15-20$ mJ/mol K^2 and $\Delta = 20$ meV results in the prediction $\alpha = k'[(0.2-0.3)$ mJ/mol K$^3]$, while the fit gives $\alpha = 0.11$ mJ/mol K^3. Comparing these numbers suggests $k' < 1$, that is, that the DOS near the nodes is less than the DOS averaged over the Fermi surface. This result is supported by recent photoemission experiments on $Bi_2Sr_2CaCu_2O_{8+\delta}$, which show an extended region of flat bands close to E_F but away from the nodes [20].

(3) Volovik's calculation may apply to strongly anisotropic s-wave superconductivity, if the minimum gap $\Delta_{\min}$ is smaller than the temperature range 2–7 K, or $\Delta_{\min} \lesssim 0.5$ meV. The limit set by photoemission is $\Delta_{\min} \leq 3$ MeV [21].

Previous authors who have identified an increase in γ with field have generally assumed a linear field dependence $\gamma(H) = [d\gamma/dH]H$ [12]. In conventional s-wave superconductors, there is a term in the specific heat proportional to the volume of normal material in the cores, $\gamma(H) = \gamma_n[H/H_{c2}]$ [22]. In YBCO, where the coherence length $\xi_0 \cong 17$ Å, the energy level spacing of the quasiparticles confined to the vortex cores can be estimated from the uncertainty principle as $\varepsilon_0 \cong \hbar^2/2m_e\xi_0^2 = k_B 150$ K [8,9]. Karrai *et al.* have found evidence for such a high core excitation energy [9]. With $\varepsilon_0 \gg k_BT$, the contribution to the specific heat from quasiparticles in the core obeys $c_{\text{core}} \propto \exp(-\varepsilon_0/k_BT)$ [22], rather than the observed term $\gamma(H)T$. Thus, within the limits of the traditional vortex core model of Caroli, de Gennes, and Matricon [8], the mere existence of $\gamma(H)$ is most easily explained by the existence of lines of nodes in YBCO. This picture of the vortex core may eventually require revision: The exact behavior of the quasiparticles in high-T_c vortex cores has not been calculated for any of the proposed gap symmetries. Even if the vortex core does prove to have a finite density of states at the Fermi level, one would expect the contributions from quasiparticles confined to the vortex core to be proportional to the number of vortices and hence linear in field.

Thermodynamic measurements cannot distinguish between different types of line nodes, and our results can be explained either by d wave or by other theories which have lines of nodes, such as extended s wave [23].

In conclusion, we have measured the specific heat of a 2.6 mg single crystal of $YBa_2Cu_3O_{6.95}$, grown by the same technique as those which have shown linear temperature dependence of the penetration depth. The magnetic field dependence of the specific heat agrees quantitatively with the field and temperature dependence predicted for the electronic specific heat of a clean superconductor with lines of nodes in the gap.

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[1] See, e.g., B. G. Levi, Phys. Today **46**, No. 5, 17 (1993).
[2] W. N. Hardy *et al.*, Phys. Rev. Lett. **70**, 3999 (1993).
[3] J. Annett *et al.*, Phys. Rev. B **43**, 2778 (1991).
[4] M. Prohammer *et al.*, Phys. Rev. B **47**, 15 152 (1993).
[5] D. Scalapino (private communication).
[6] R. B. Laughlin (private communication).
[7] G. E. Volovik, JETP Lett. **58**, 469 (1993).
[8] C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Lett. **9**, 307 (1964).
[9] K. Karrai *et al.*, Phys. Rev. Lett. **69**, 152 (1992).
[10] Ruixing Liang *et al.*, Physica (Amsterdam) **195C**, 51 (1992).
[11] J. S. Urbach *et al.*, Phys. Rev. B **39**, 12 391 (1989), and references therein.
[12] For reviews, see, e.g., N. E. Phillips *et al.*, in *Progress in Low Temperature Physics XIII*, edited by D. F. Brewer, (North-Holland, Amsterdam, 1992); A. Junod, in *Physical Properties of HTSC II*, edited by D. Ginsberg (World Scientific, Singapore, 1990).
[13] A. P. Ramirez *et al.*, Mater. Res. Soc. Symp. Proc. **99**, 459 (1987).
[14] K. A. Moler *et al.* (to be published).
[15] F. Mehran *et al.*, Solid State Commun. **67**, 55 (1988).
[16] J. W. Loram et al., Phys. Rev. Lett. **71**, 1740 (1993).
[17] J. P. Emerson *et al.*, Phys. Rev. B **49**, 9256 (1994).
[18] T. E. Mason *et al.*, Phys. Rev. Lett. **71**, 919 (1993).
[19] D. Sanchez *et al.*, Physica **200**, 1 (1992).
[20] D. S. Dessau *et al.*, Phys. Rev. Lett. **71**, 2781 (1993).
[21] Z.-X. Shen *et al.*, Phys. Rev. Lett. **70**, 1553 (1993).
[22] A. L. Fetter and P. C. Hohenberg, in *Superconductivity*, edited by R. D. Parks (M. Dekker, New York, 1969).
[23] C. M. Varma (private communication); P. B. Littlewood *et al.*, Phys. Rev. Lett. **63**, 26 002 (1989).