# Low-temperature specific heat of polycrystalline $YBa_2Cu_3O_{6.70}$ in applied magnetic fields of 0, 1, 2, and 3 T

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We have measured the specific heat of sintered $YBa_2Cu_3O_{6.70}$ powder between 1.85 and 77 K in zero magnetic field, and between 1.75 and 9.5 K in applied fields up to 3 T. The sample was characterized by x-ray diffraction, scanning electron microscopy, iodometric titration, and magnetic susceptibility. The onset of the diamagnetic transition to the superconducting state occurred at $T_c=67$ K. For the specific heat in nonzero applied magnetic field, there is an increase in the magnitude of the term that is linear in temperature, and a decrease in the term that is cubic in temperature. These results agree with earlier results on the $T_c=90$ K phase of $YBa_2Cu_3O_{7-\delta}$. The data for nonzero applied fields were analyzed by using Ginzburg-Landau theory in the London limit for a uniaxially symmetric superconductor.

## I. INTRODUCTION

The interpretation of the low-temperature specific heat of $YBa_2Cu_3O_{7-\delta}$ is still uncertain. Several features, including the presence of a term with a linear dependence on temperature in zero applied magnetic field, $\gamma_0 T$, for polycrystalline samples, and a term with a possible fractional power dependence on temperature for single-crystal samples,[1,2] remain unexplained. Based on the smaller linear term (at least an order of magnitude smaller) in the Bi and Tl systems,[2] it appears that a linear term is not necessarily associated with high-temperature superconductivity. Several recent explanations for the low-temperature specific heat include limited volume fraction of superconductivity[3,4] and spin excitations (including spin-glass[5,6] and antiferromagnetic correlations[7,8]).

Baak *et al.*[8] were able to reconcile most of the data for 90-K single crystals by using a model based on one-dimensional Heisenberg spin-$\frac{1}{2}$ random antiferromagnetic exchange.[9] The polycrystalline data of Reeves *et al.*[10] are not in good agreement with this model, though Baak *et al.* point out that, for the range of temperatures and fields used by Reeves *et al.*, it would be difficult to observe the effects of the antiferromagnetic exchange. By applying their model to the data of Reeves *et al.*, Baak *et al.* found more reasonable values of the penetration depth than Reeves *et al.* did.

The 60-K phase of $YBa_2Cu_3O_{7-\delta}$ has a lower carrier density than the 90-K phase and is thought to contain some deoxygenated Cu-O chains.[11] Studies of the specific heat of $YBa_2Cu_3O_{7-\delta}$ as a function of $\delta$ have been somewhat inconclusive. No clear correlation between $\gamma_0$ and $\delta$ has been observed; $\gamma_0$ has been variously reported to increase, decrease, and stay the same as $\delta$ is increased.[2] The Debye temperature, $\Theta_D$, has been reported to decrease as oxygen is removed.[2] We have measured the specific heat of $YBa_2Cu_3O_{6.7}$ at low temperatures and in magnetic fields up to 3 T in an attempt to gain more information regarding the linear term and the bulk properties of the superconducting state and the mixed state.

## II. EXPERIMENTAL METHOD

### A. Sample preparation

High-quality starting powders and pellets of 90-K $YBa_2Cu_3O_{7-\delta}$ were prepared as described previously.[10] Oxygen was removed from the 90-K sample by using a zirconium foil gettering technique.[12] The sintered 90-K sample was sealed under vacuum in a quartz tube containing zirconium foil, and the sealed tube was placed in a furnace at 415 °C for 5 days. The quartz tube was then quenched into liquid nitrogen.

### B. Characterization

The oxygen content of a 0.3-g section of the sample was determined by iodometric titration. Analyzing two pieces, the oxygen contents were determined to be 6.695 and 6.696±0.005 per formula unit.

The x-ray-diffraction pattern showed that our 60-K sample was nearly single phase. There were only a few spurious peaks. We saw evidence (just above our detection limits) of BaO and traces of the $T_c=90$-K phase of $YBa_2Cu_3O_{7-\delta}$. No other impurities were observed (indicating an upper limit of a few atomic %). We fitted 42 peaks to obtain the lattice constants $a=3.822$ Å, $b=3.888$ Å, and $c=11.663$ Å. These lattice constants are in agreement with published values[13,14] for an oxygen stoichiometry of 6.7. The orthorhombic distortion $2(b-a)/(a+b)$ was 0.0171, and the unit-cell volume $V$ was 173.3104 Å$^3$. The ideal density $\rho$ was 6.3336 g/cm$^3$, and our sample had a density of about 75% of that value.

 

### C. Magnetic susceptibility

The superconducting and normal-state magnetic properties were studied in an applied magnetic field of 10.87 Oe. The magnetic moment was measured after zero-field cooling and field cooling. The susceptibility $\chi$ was calculated assuming the ideal density; no corrections for demagnetizing effects were made. The susceptibility data are shown in Fig. 1. The transition temperature $T_c$ was 67 K (onset of superconducting state), and the width $\delta T_c$ (10–90 %) was 28 K. The Meissner fraction (field cooled) at 5 K was 33% of the ideal value $-1/4\pi$, and the shielding fraction (zero-field cooled) at 5 K was 60% of $-1/4\pi$. The zero-field-cooled values have an accuracy of $\pm 10\%$ because a 1-Oe field may have been trapped in the magnetometer.

The observed transition width and Meissner fraction are similar to those seen in our 90-K polycrystalline samples.[10] The shielding fraction appears to be lower in magnitude than that of our 90-K samples. One possible explanation for the low shielding fraction would be a lower critical current density in the 60-K phase, but the current density $j$ needed to screen a field of 10 Oe is well below the estimates of the critical current density $j_c$ of this material.[15] Another explanation would be a lower intergranular critical field $H_{c1}^*$ in the 60-K material, as observed in polycrystalline samples of the 90-K phase.[16] Yet another possibility would be inhomogeneity in the oxygen content of the sample.

We repeated the zero-field-cooled measurement at 5 K in an applied field of 13 Oe and then 50 Oe. The shielding fraction at 50 Oe was 4% less than the fraction at 13 Oe. (We note that 100% shielding fractions have been observed by others in 60-K single crystals.[17]) If we could apply a magnetic field less than $H_{c1}^*$, we would presumably observe shielding fractions close to the ideal value of $-1/4\pi$.

We needed to verify that the applied magnetic field would not be distorted by the superconducting sample. Measurements of susceptibility are shown in Fig. 2. The fraction of the field penetrating the sample, given by the ratio

$$\frac{B}{H} = 1 + 4\pi\chi ,$$

is close to unity for the range of temperatures and fields to be used. The magnetic field is therefore essentially undisturbed by the sample.

Finally, we measured the normal-state susceptibility of our sample between 70 and 300 K in an applied field of 0.5 T. (The sample holder's susceptibility was used to correct the data.) The data were fit to

$$\chi = \chi_0 + \frac{C}{T} ,$$

between 80 and 220 K. We found $\chi_0 = 2.478 \times 10^{-6}$ and $C = 1.399 \times 10^{-4}$ K. The lowest-temperature value was not included in the fit, to minimize contributions from superconducting fluctuations. A plot of $\chi T$ versus $T$ is shown in Fig. 3. The deviation of the point at 70 K from the straight line is a signal of superconducting fluctuations. Using the determined value of $C$, and assuming that the paramagnetic behavior is associated with permanent magnetic moments on Cu atoms, each of magnitude $1.5\mu_B$, we calculate the ratio of the number of $Cu^{2+}$ to the number of Cu atoms to be 20%. In the 90-K phase, the presence of a large number of $Cu^{2+}$ atoms is

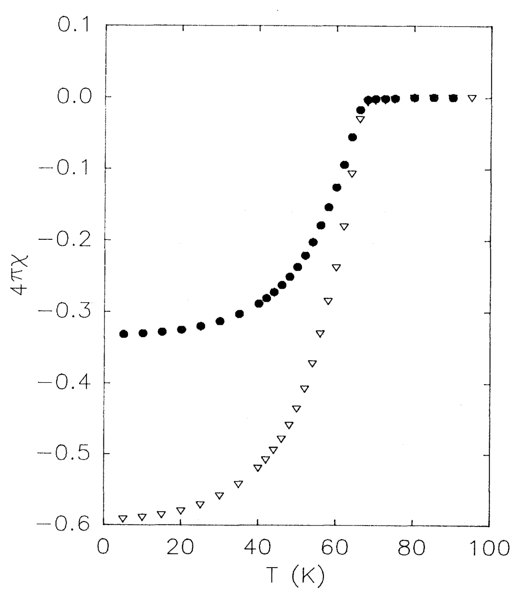


FIG. 1. The magnetic susceptibility (Gaussian units) vs temperature in the superconducting state. The applied magnetic field was 10.87 Oe. The circles show field-cooled data, and the triangles show zero-field-cooled data.

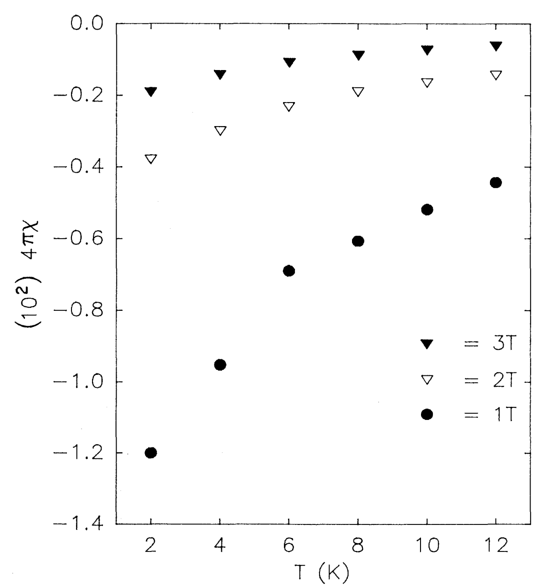


FIG. 2. The magnetic susceptibility of our sample taken in high fields (Gaussian units). The sample was zero-field cooled, and the data were taken while warming in the field. The data show that the shielding of the sample was negligible for the field strengths used in our experiment.

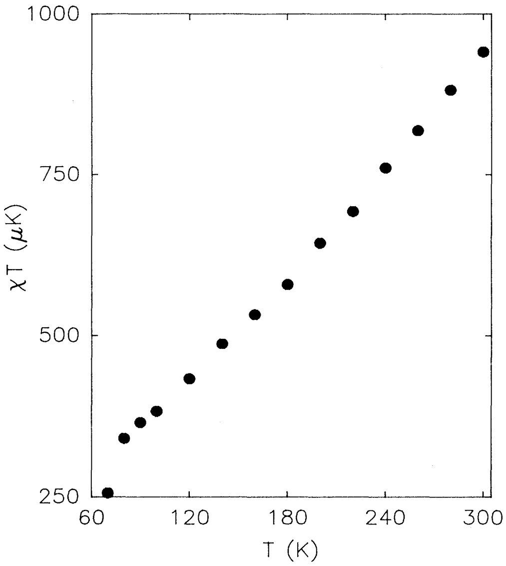


FIG. 3. The normal-state magnetic susceptibility of our sample (Gaussian units) times temperature. The applied field was 0.5 T.

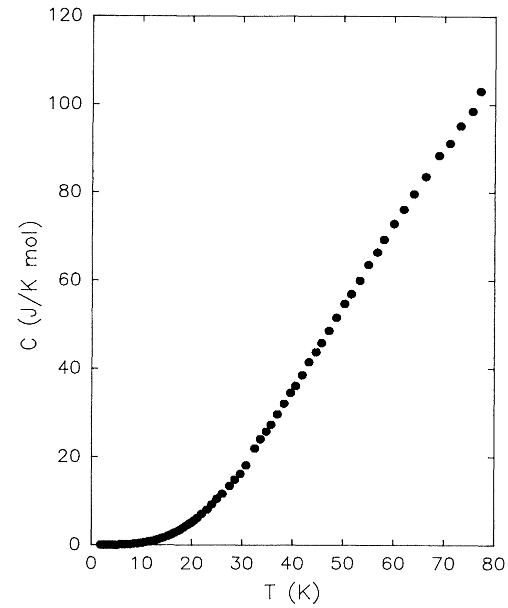


FIG. 4. The specific heat of our sample in zero applied field.

usually associated with an impurity phase. However, the permanent magnetic moments on the Cu atoms in our sample may have been created as oxygen was removed from the sample to reduce the transition temperature, as observed by several authors.[18]

### D. Heat capacity

We measured the heat capacity of a 2.7-g sample of $YBa_2Cu_3O_{6.70}$ from 1.9 to 77 K in zero applied magnetic field, and from 1.75 to 9.5 K in applied fields of 1, 2, and 3 T. The heat capacity was measured as described previously.[10,19,20]

The data were averaged in groups of 4 data points to reduce scatter. The specific heat from 1.9 to 77 K in zero applied field is shown in Fig. 4. The low-temperature specific heat in zero applied field is shown in Fig. 5. The low-temperature specific heat in zero and nonzero applied fields are shown in Fig. 6.

The low-temperature data in zero applied field show a linear behavior in a $C/T$ versus $T^2$ plot between 5 and 9 K. Below 5 K and above 9 K, the data deviate from this linear behavior. Plots of $C/T^3$ versus $T$ show a peak between 20 and 30 K, which is consistent with dispersion in the phonon spectrum.[21] The size of the upturn below 3 K increases with field strength. This is a characteristic of a Schottky anomaly; its presence is in agreement with the observed Curie behavior in the normal-state susceptibility. There was no observable jump in the specific heat at $T_c$, consistent with the very small heat jump $\Delta C = 0.2$ mJ/mol K observed by Ghiron *et al.*,[22] which is below the resolution of our apparatus.

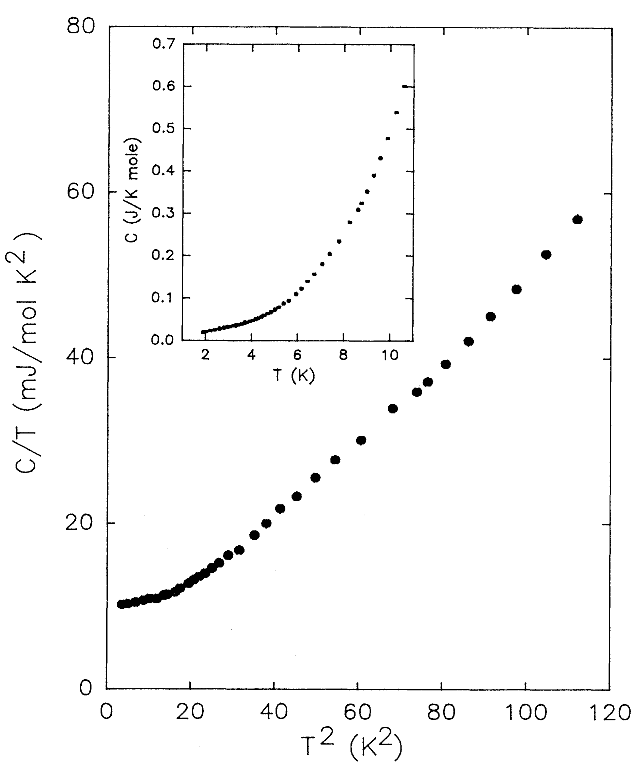


FIG. 5. The low-temperature specific heat of our sample in zero applied field plotted as $C/T$ vs $T^2$. Inset: The low-temperature specific heat of our sample in zero applied field plotted as $C$ vs $T$.

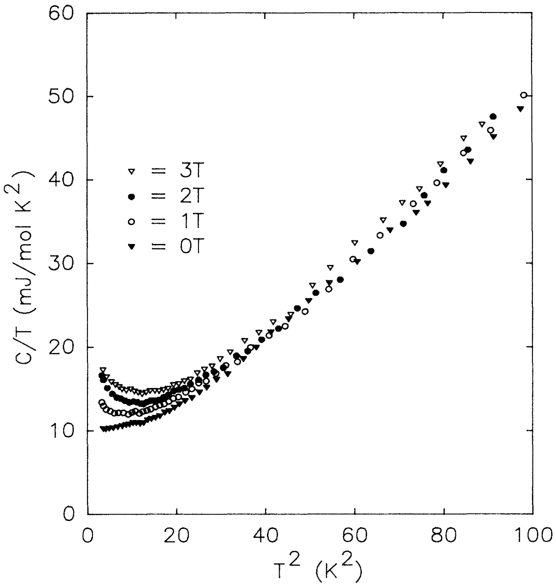


FIG. 6. The low-temperature specific heat of our sample in zero and nonzero applied field plotted as $C/T$ vs $T^2$.

## III. ANALYSIS

The low-temperature zero-field specific heat was fit to several functions over various temperature ranges, minimizing $\chi^2$, defined by

$$\chi^2=\sum_i\left[\frac{C_{i,\mathrm{data}}-C_{i,\mathrm{fit}}}{C_{i,\mathrm{data}}}\right]^2 .$$

This choice of fitting criterion gives equal weighting to all the data points. The results of our fits are given in Table I. The best fit is

$$C=AT^{-2}+\gamma_0T+\beta_0T^3$$

with

$$A=(4.10\pm1.23)\times10^{-2}\ \mathrm{J\,K/mol}\ ,$$

$$\gamma_0=(4.71\pm0.80)\times10^{-3}\ \mathrm{J/mol\,K^2}\ ,$$

$$\beta_0=(4.11\pm0.26)\times10^{-4}\ \mathrm{J/mol\,K^4}$$

(corresponding to a Debye temperature of 392 K), and $\chi^2=2.3\times10^{-3}$. The uncertainty in the fitting parameters was determined by incrementing the parameter of interest and varying the other fit parameters, with a criterion of 99% certainty.[23] We note that the data could not be fit with only a simple Schottky term and a Debye term.

Our results are within the range of values that have been reported previously in the literature[2] and with recent measurements.[24] The linear term is larger and the cubic term is smaller than the values previously measured by us on 90-K powders.[10]

The data can also be fit to

$$C=FT^n+\beta_0T^3\ ,$$

which is similar to the functional form used by Baak *et al.*[8] to fit the low-temperature specific heat of 90-K single crystals of $YBa_2Cu_3O_{7-\delta}$. Our best fit has $n=0.13\pm0.167$. For 90-K single crystals, Baak *et al.* found $n\approx0.4$. The value of $n$ we determine is very sensitive to the range of temperatures used in the fit, and we do not have enough data at low enough temperatures to determine $n$ with adequate precision. We therefore do not find it useful to analyze our data with the model of Baak *et al.*[8]

There have been many measurements of the low-temperature specific heat of polycrystalline phase $YBa_2Cu_3O_{7-\delta}$.[2] A linear term, a Debye term, and sometimes a Schottky term are usually used to fit the data. There is a significant spread in the published results (most likely reflecting sample variations) with no clear dependence of the linear term on the mean oxygen content, $7-\delta$: $\gamma_0$ has been variously observed to increase, decrease, and remain the same as $\delta$ is increased. We speculate that the linear dependence on temperature seen in 60-K and 90-K polycrystalline samples and the fractional power-law dependence on temperature seen in 90-K single crystals have a common origin: interactions in a disordered medium. The disorder may be associated with the spatial distribution of oxygen in the sample along the Cu-O chains, possibly occuring on a scale comparable to the unit-cell dimensions.[25] The absence of a clear dependence of $\gamma_0$ on the mean oxygen content and the variation of $\gamma_0$ from sample to sample may be caused by the disorder, rather than by the mean oxygen content of the sample. The added term in the low-temperature specific heat is caused by interactions between excitations which are partially localized on the sites of disorder.

This type of interpretation is similar to the theory of the metal-insulator transition,[26,27] where interactions between localized electrons lead to a specific heat with a dependence on temperature varying from a fractional

TABLE I. Fits to our data in zero applied field. The coefficient of the linear term $\gamma_0$ in mJ/mol K$^2$, other coefficients in the fits to the low-temperature specific heat in units of mJ/mol K$^x$ ($x$ varies depending on the order of the term), $n$ the power of temperature in fit 1, is dimensionless, the temperature range over which fits were made to the data in K, $\Theta_D$ the Debye temperature in K, and $\chi^2$ is dimensionless. 1 is $C=FT^n+\beta_0T^3$ and 2 is $C=AT^{-2}+\gamma_0T+\beta_0T^3$.

| Fit | Coefficients | $\Theta_D$ | Range | $10^3\ \chi^2$ |
|---|---|---|---|---|
| 1 | $F=16.12\pm2.6$<br>$n=0.132\pm0.167$<br>$\beta_0=0.441\pm0.02$ | 383 | 1.9–9 | 1.02 |
| 2 | $A=41.0\pm12.3$<br>$\gamma_0=4.71\pm0.8$<br>$\beta_0=0.411\pm0.026$ | 392 | 2–10 | 2.28 |

power to linear behavior, depending on the strength of the interaction and the temperature.[28] Such a model of localized states is consistent with the absence of a linear dependence on temperature in thermal conductivity measurements.[2] In more homogeneous samples, the size of the effect would presumably be reduced, although some inhomogeneity is characteristic of samples produced by currently available techniques, and it may be intrinsic to materials with the perovskite structure.

We note that our suggestion is very similar to those made by Baak *et al.*,[8] who analyzed the fractional power of temperature observed in their low-temperature specific-heat data on 90-K single crystals with a model of one-dimensional Heisenberg spin-$\frac{1}{2}$ random antiferromagnetic exchange.[9] The specific interaction mechanism proposed by Baak *et al.*[8] has not been proven. Specific-heat measurements alone cannot determine the interaction mechanism. However, our proposal contains essentially the same physics: interactions in a disordered medium.

The low-temperature specific-heat data in nonzero applied magnetic field were fit to

$$C = AT^{-2} + \gamma T + \beta T^3 .$$

The results of these fits are given in Table II. We define $\gamma = \gamma_0 + \gamma(H)$ and $\beta = \beta_0 + \beta(H)$, with

$$\gamma_0 = 4.71 \text{ mJ/mol K}^2 ,$$

$$\beta_0 = 0.411 \text{ mJ/mol K}^4 ,$$

and $\gamma(H=0)$ and $\beta(H=0)$ are defined to be zero. A plot of $\gamma(H)$ and $\beta(H)$ versus $H$ is shown in Fig. 7. The rate of increase of $\gamma$ with $H$ is approximately the same as the value observed by us previously for 90-K powders,[10] and the rate of decrease of $\beta$ with $H$ is approximately half the

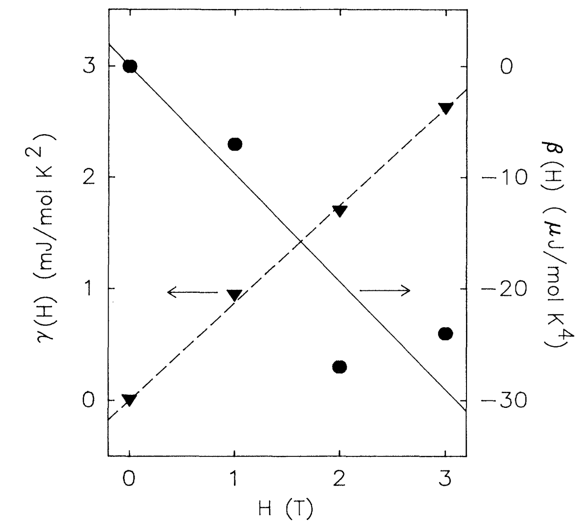


FIG. 7. The coefficients $\gamma(H)$ (solid triangles) and $\beta(H)$ (solid circles) from fits to the low-temperature specific heat, plotted as a function of the applied magnetic field strength $H$. The dotted and solid lines are fits to the data.

value observed by us previously for 90-K powders.[10] Chernoplekov *et al.*[29] measured the low-temperature specific heat of oxygen-reduced $YBa_2Cu_3O_{7-\delta}$ in zero applied field and in an applied field of 8 T. Their sample had a transition temperature of 54 K and $\delta = 0.3$. They determined that the specific heat increased with field above 4 K and that this increase becomes weaker as the mean oxygen content of the sample is reduced, in agreement with our results. For temperatures below 4 K, Chernoplekov *et al.* observed a down turn in the specific heat in applied magnetic field, in contrast to our results.

Given the inherent uncertainty in a three-parameter fit with terms that are not mutually orthogonal, and the possibility that the low-temperature data (below 3 K) might be described by a term which goes as $T^n$ $(0 < n < 1)$, as opposed to $T^{-2}$, we fit our data from 5 to 8 K (where the $T^{-2}$ or $T^n$ term do not make a significant contribution) to

$$C = \gamma T + \beta T^3 .$$

The values of $\gamma$ and $\beta$ are in good agreement (within the reported uncertainties) with the values determined in our reported fits to the data.

To verify that our qualitative results that $\gamma(H)$ is positive and $\beta(H)$ is negative, do not depend on the assumption that the phonon contribution to the specific heat goes as $\beta T^3$, we also fit our data to

$$C = AT^{-2} + \gamma T + \beta T^3 + DT^5 .$$

While the magnitude of $\gamma(H)$ and $\beta(H)$ are larger for this fitting function, $\gamma(H)$ is still positive and $\beta(H)$ is still negative. The Debye temperature determined from the fit to the zero-field data for this fitting function ($\Theta_D = 462$ K) is large compared to the values measured by other groups.[2] Therefore, we did not use values for $\gamma(H)$ and $\beta(H)$

TABLE II. Fits to our data in nonzero applied field. The applied magnetic field $H$ in T, the coefficient of the linear term $\gamma$ in mJ/mol K$^2$, other coefficients in the fits to the low-temperature specific heat in units of mJ/mol K$^x$ ($x$ varies depending on the order of the term), the temperature range over which fits were made to the data in K, $\Theta_D$ the Debye temperature in K, and $\chi^2$ is dimensionless.

| $H$ | Coefficients[a,b,c] | $\Theta_D$ | Range | $10^3$ $\chi^2$ |
|---|---|---|---|---|
| 1 | $A = 56.4 \pm 16.5$ | 394 | 2–10 | 2.596 |
| | $\gamma = 5.65 \pm 0.99$ | | | |
| | $\beta = 0.404 \pm 0.031$ | | | |
| 2 | $A = 80.5 \pm 19.0$ | 401 | 2–9.5 | 2.012 |
| | $\gamma = 6.40 \pm 1.0$ | | | |
| | $\beta = 0.384 \pm 0.031$ | | | |
| 3 | $A = 84.1 \pm 21.6$ | 400 | 2–9 | 2.622 |
| | $\gamma = 7.33 \pm 1.23$ | | | |
| | $\beta = 0.387 \pm 0.038$ | | | |

[a] $C = AT^{-2} + \gamma T + \beta T^3$.
[b] $\gamma = \gamma_0 + \gamma(H)$, where $\gamma_0 = 4.71$ mJ/mol K$^2$ and $\gamma$ $(H=0)$ is defined to be zero.
[c] $\beta = \beta_0 + \beta(H)$, where $\beta_0 = 0.441$ mJ/mol K$^2$ and $\beta$ $(H=0)$ is defined to be zero.

determined for this fitting function in our analysis.

The field dependence of a uniaxial symmetric superconductor in the London limit has been calculated by Reeves *et al.*[10] using Ginzburg-Landau theory.[30] In this model the field dependence of the specific heat is caused by changes in the local magnetic field and the kinetic energy of the superconducting electrons which screen these magnetic vortices. This model neglects the contribution made by the normal electrons in the core of the magnetic vortices (because the vortex radii are so small).

The field dependence of the heat capacity caused by the presence of magnetic vortices in the superconducting state is, to lowest order,[10]

$$C=\gamma(B)T+\beta(B)T^3+\cdots .$$

$\gamma(B)$ and $\beta(B)$ are defined in Ref. 10. Higher-order terms in the expansion for the heat capacity are of order $(B/H_{c2})^2$. Using this model, Reeves *et al.*[10] were unable to obtain reasonable values for the penetration depth for the 90-K phase of $YBa_2Cu_3O_{7-\delta}$ in terms of the experimental values for the mass anisotropy and their specific-heat data.

We attempt a similar analysis for our 67-K sample, using the coefficients $\gamma(H)$ and $\beta(H)$ determined from our field-dependent specific-heat data. We fit $\gamma(H)$ versus $H$ to a straight line (see Fig. 7). Note that $H\approx B$ since the magnetization of the sample is very small. We find that

$$\gamma(B)/B=0.87\ \mathrm{mJ/(mol\,T\,K^2)}\ .$$

Similarly,

$$\beta(B)/B=-9.67\ \mu\mathrm{J/(mol\,T\,K^4)}\ .$$

From the calculated form of $\gamma(B)$ and the fact that the determinant of the effective mass tensor equals 1 ($m_1^2 m_3=1$, $m_3$=the $c$-axes effective mass, $m_1$=the effective mass along the $a$ and $b$ axes, which are approximated as being equal), we find that the penetration depth with the applied field along the $c$ axis is

$$\lambda(0)\sqrt{m_1}=\left\{\frac{B\Phi_0 a}{\gamma(B)32\pi^2T_c^2}\left[1+\frac{1}{2\alpha(\alpha^2-1)^{1/2}}n\left[\frac{\{\alpha+[(\alpha^2-1)]^{1/2}\}}{\{\alpha-[(\alpha^2-1)]^{1/2}\}}\right]\right]\right\}^{1/2},$$

where $B$ is the magnetic field, $\Phi_0$ is the magnetic flux quantum, $a=1+0.43/1.77$ (in the clean limit), $\alpha^2=m_3/m_1$. We are unaware of any measurements of the mass anisotropy for 60-K or 67-K $YBa_2Cu_3O_{7-\delta}$. Recent work on the 90-K phase by Farrell *et al.*[31] determined that the mass anisotropy $\alpha=7.9\pm0.2$. We calculate the penetration depth with the magnetic field along the $c$ axis for $4\le\alpha\le10$, using $\gamma(B)/B$ in Gaussian units, scaled by the density and the atomic weight:

$$\gamma(B)/B=8.37\times10^{-3}\ \mathrm{ergs/G\,K^2\,cm^3}$$

The penetration depth varies from 495 to 472 Å for $\alpha=4-10$. These penetration depths are lower than the measured values for 60 (Ref. 32) and 90-K (Refs. 33 and 34) samples, as in the work of Reeves *et al.*[10]

$H_{c2}$ has not been measured but is thought to be extremely large. To obtain a lower bound on $\gamma(B)/\beta(B)$, we assume that $H_{c2}/B=1000T/1T$. From the expression in Ref. 10 the value of $\gamma(B)/\beta(B)$ is then 144.2 $\mathrm{K}^2$. From our data, $\gamma(B)/\beta(B)=-90.4$; it has the wrong sign and is too small in magnitude.

There are several possible explanations for the disagreements between the theory and our experimental results including pinning of vortices, variations in the long-wavelength phonon spectrum with magnetic field, vortex entanglement, vortex dynamics, quasiparticle excitations, and magnetic excitations.

Two possible explanations for the observed negative value of $\beta(B)$ are magnetic excitations and/or quasiparticle excitations. In order for quasiparticles to contribute to the specific heat at these low temperatures, the pairing state would have to be unconventional (possessing point or line nodes). Annet *et al.*[35] discuss the possible pairing states consistent with the current experimental results.

## IV. CONCLUSIONS

We have measured the low-temperature specific heat of $YBa_2Cu_3O_{6.70}$ in applied magnetic fields of 0, 1, 2, and 3 T. The best fit to the data taken in zero applied field contains a term which is linear in temperature. We speculate that the origin of the linear and the fractional power of temperature seen in the low-temperature specific heat of the these compounds are due to interactions in a disordered medium, as predicted by the theory of the metal-insulator transition.[26,27] The theory[9] used by Baak *et al.*[8] represents a particular choice of interaction mechanism.

We have analyzed the low-temperature specific-heat data taken in the applied field (1, 2, and 3 T) using Ginzburg-Landau theory in the London limit for a uniaxially symmetric superconductor.[10,30] The theory was able to account for only part of the enhancement of the linear term in a magnetic field and was unable to account for the reduction of the cubic term with field. Our results are qualitatively similar to those of Reeves *et al.*[10] for 90-K powders and to those of Chernoplekov *et al.*[29] for oxygen-reduced powders.

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[1]S. E. Stupp and D. M. Ginsberg, Physica C **158**, 299 (1989).

[2]A. Junod, in *The Physical Properties of High Temperature Superconductivity II,* edited by D. M. Ginsberg (World-Scientific, Singapore, 1990), Chap. 2.

[3]N. E. Phillips, R. A. Fisher, J. E. Gordon, S. Kim, A. M. Stacy, M. K. Crawford, and E. M. McCarron III, Phys. Rev. Lett. **65**, 357 (1990).

[4]A. Junod, D. Eckert, T. Graf, G. Triscone, and J. Muller, Physica C **162**, 1401 (1989).

[5]J. S. Urbach, D. B. Mitzi, A. Kapitulnik, J. Y. T. Wei, and D. E. Morris, Phys. Rev. B **39**, 12 391 (1989).

[6]R. Caspary, M. Winkelmann, and F. Steglich, Z. Phys. B **77**, 41 (1989).

[7]J. Baak, C. J. Muller, H. B. Brom, M. J. V. Menken, and A. A. Menovsky (unpublished).

[8]J. Baak, C. J. Muller, H. B. Brom, M. J. V. Menken, K. Kadowaki, and A. A. Menovsky, Physica C **168**, 363 (1990).

[9]L. N. Bulaevskii, A. V. Zvarykina, Y. S. Karimov, R. B. Lyubovskii, and I. F. Shchegolev, Zh. Eksp. Teor. Fiz. **42**, 725 (1972) [Sov. Phys. JETP **35**, 384 (1972)]; L. N. Bulaevskii, A. A. Gusseinov, O. N. Eremenko, V. N. Topnikov, and I. F. Shchegolev, Fiz. Tverd. Tela (Leningrad) **17**, 781 (1975) [Sov. Phys. Solid State **17**, 498 (1975)].

[10]M. E. Reeves, S. E. Stupp, T. A. Friedmann, F. Slakey, D. M. Ginsberg, and M. V. Klein, Phys. Rev. B **40**, 4573 (1989).

[11]R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. P. Parkin, M. L. Ramierez, K. P. Roche, J. E. Vasquez, T. M. Gur, and R. A. Huggins, Nature **340**, 619 (1989).

[12]R. J. Cava, B. Batlogg, C. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Nature **329**, 423 (1987).

[13]R. M. Hazen, *The Physical Properties of High Temperature Superconductivity II* (Ref. 2), Chap. 3.

[14]K. Kadowaki, Y. K. Huang, M. van Sprang, and A. A. Menovsky, Physica B and C **145**, 1 (1987).

[15]A. P. Malozemoff, in *The Physical Properties of High Temperature Superconductivity I,* edited by D. M. Ginsberg (World-Scientific, Singapore, 1989), Chap. 3.

[16]For example, S. Senoussi, S. Hadjoudj, R. Maury, and A. Fert, Physica C **165**, 364 (1990).

[17]J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Low Temp. Phys. **77**, 119 (1989).

[18]Y. Nakazawa and M. Ishikawa, Physica C **158**, 381 (1989); Y. Yamaguchi, M. Tokumoto, S. Waki, Y. Nakagawa, and Y. Kimura, Phys. Soc. Jpn. **58**, 2256 (1989); D. C. Johnston, S. K. Sinha, A. B. Jacobson, and J. M. Newsam, Physica C **153-155**, 572 (1988).

[19]M. E. Reeves, Ph.D. thesis, University of Illinois at Urbana-Champaign, 1989.

[20]S. E. Stupp (unpublished).

[21]A. Junod, T. Jarlborg, and J. Muller, Phys. Rev. B **27**, 1568 (1983).

[22]K. Ghiron (private communication).

[23]P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), Chap. 10.

[24]S. J. Collocott, R. Driver, and E. R. Vance, Phys. Rev. B **41**, 6329 (1990); Y. Nakazawa, J. Takeya, and M. Ishikawa (unpublished).

[25]The proposal that the added contribution to the specific heat is associated with states localized on oxygen vacancies was made previously by others and is summarized in Ref. 2.

[26]C. Castellani and C. Di Castro, Phys. Rev. B **34**, 5935 (1986).

[27]C. Castellani, G. Kotliar, and P. A. Lee, Phys. Rev. Lett. **59**, 323 (1987).

[28]In this model, the linear dependence on temperature is due to the excitation of electrons at the Fermi surface. This notion, in its simple form, is not appropriate for a superconductor. We do not propose to simply apply the theory of Castellani *et al.* to a superconductor. Instead, we emphasize the underlying physics of interactions in a disordered medium.

[29]N. A. Chernoplekov, M. H. Khlopkin, G. K. Panova, P. P. Parshin, B. I. Saveljev, A. A. Shikov, and M. G. Zemljanov, Physica C **153-155**, 1655 (1988).

[30]V. Kogan, Phys. Rev. B **24**, 1572 (1981); L. J. Campbell, M. M. Doria, and V. G. Kogan, *ibid.* **38**, 2439 (1988).

[31]D. E. Farrell, J. P. Rice, D. M. Ginsberg, and J. Z. Liu, Phys. Rev. Lett. **64**, 1573 (1990).

[32]Y. J. Uemura, J. Appl. Phys. **64**, 6087 (1988).

[33]D. R. Harshman, L. F. Schneemeyer, J. V. Waszczak, G. Aeppli, R. J. Cava, B. Batlogg, and L. W. Rupp, Phys. Rev. B **39**, 851 (1989).

[34]L. Krusin-Elbaum, R. L. Greene, F. Holtzberg, A. P. Malozemoff, and Y. Yeshurun, Phys. Rev. Lett. **62**, 217 (1989).

[35]J. F. Annett, N. Goldenfeld, and S. R. Renn, *The Physical Properties of High Temperature Superconductivity II* (Ref. 2), Chap. 9.