Direct Observation and Anisotropy of the Contribution of Gap 

nodes in the Low Temperature Specific Heat of YBa$_2$Cu$_3$O$_7$

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Abstract

The specific heat due to line nodes in the superconducting gap of YBa$_2$Cu$_3$O$_7$ has been blurred up to now by magnetic terms of extrinsic origin, even for high quality crystals. We report the specific heat of a new single crystal grown in a non-corrosive BaZrO$_3$ crucible, for which paramagnetic terms are reduced to $\approx 0.006\%$ spin-1/2 per Cu atom. The contribution of line nodes shows up directly in the difference $C(B, T) - C(0, T)$ at fixed temperatures ($T < 5$ K) as a function of the magnetic field parallel to the $c$-axis ($B \leq 14$ T). These data illustrate the smooth crossover from $C \propto T^2$ at low fields to $C \propto TB^{1/2}$ at high fields, and provide new values for gap parameters which are quantitatively consistent with tunneling spectroscopy and thermal conductivity in the framework of $d_{x^2-y^2}$ pairing symmetry. Data for $B$ along the nodal and antinodal directions in the $ab$-plane are also provided. The in-plane anisotropy predicted in the clean limit is not observed.
I. INTRODUCTION

Many experiments tend to establish that the symmetry of the order parameter in high temperature superconductors (HTS) is $d_{x^2-y^2}$, with a possible minor $s$-wave admixture [1,2]. Whether they probe the amplitude or the phase of the order parameter, these measurements have been generally restricted to the surface of the samples. Alternatively, specific heat ($C'$) experiments have been used to search for bulk evidence of a non-conventional gap, taking advantage of their sensitivity to the low energy excitations of a system. In a $d_{x^2-y^2}$ superconductor, the gap $\Delta(\vec{k})$ vanishes and changes sign on lines of nodes in $k$-space. The finite slope of the gap at the nodes causes a linear increase of the density of states (DOS) at low energy, $N(E) \propto |E|$. As the electronic part of $C/T$ is proportional to the DOS averaged over an interval $\approx k_B T$ about the Fermi level, it follows that $C_{\text{electron}}/T = \alpha T$ at $T \ll T_c$ in zero magnetic field. This contrasts with the exponential law $C_{\text{electron}}/T \propto T^{-2.5} exp(-\Delta_0/T)$ that would apply at very low temperature to a fully-gapped $s$-wave superconductor.

In a magnetic field, the energy of carriers circulating around a vortex is shifted by Doppler effect. This allows them to be excited above the local gap on the Fermi surface near the nodes. Detailed calculations show that a contribution $C_{\text{vortex}}/T = A_c B^{1/2}$ arises in the $T = 0$ limit [3]. In a conventional isotropic $s$-wave superconductor, no significant contribution would be expected at low temperature from such a mechanism, since a field on the order of $B_{c2}$ is needed to shift the energy by an amount comparable to the gap $\Delta_0$.

Two other mechanisms may contribute to the low temperature specific heat of superconductors in a magnetic field: the Zeeman shift [4] and localized levels in vortex cores. The Zeeman and Doppler contributions to $C/T$ scale as $B/B_{c2}$ and $(B/B_{c2})^{1/2}$, respectively, so that the latter dominates at low fields. Localized levels in vortex cores also add a contribution $\propto (B/B_{c2})$. For a low-$T_c$ superconductor with a large coherence length $\xi$, the mini-gaps $\approx \Delta_0/k_F\xi$ between these levels are so small that the local DOS can be considered as continuous; the average DOS is proportional to the area occupied by vortex cores and entails $C/T \propto (B/B_{c2})$. This is the main field-induced contribution at low temperature.
for classic superconductors. For HTS, the localization in smaller vortex cores increases the separation between levels. Tunneling spectroscopy \cite{7} tends to show that the mini-gaps are then on the order of $\approx 0.3k_BT_c$, which implies that the contribution of core levels should be negligible in the temperature range $T < T_c/20$ investigated here. Furthermore, the very existence of localized core levels for a pure $d$-wave superconductor is questionable, as they can leak along the nodal directions and mix with other states.

Summarizing, the presence of line nodes in HTS is reflected by terms $C(T \ll T_c, B = 0)/T = \alpha T$ and $C(T = 0, B \ll B_{c2})/T = A_cB^{1/2}$, whereas for a fully gapped, low temperature superconductor $C(T \ll T_c, B = 0)/T \propto \exp(-\Delta_0/T) \approx 0$ and $C(T = 0, B \ll B_{c2})/T \propto B$. However these simple criteria are not easily applied in practice because of the presence of additional contributions to the measured specific heat. In YBa$_2$Cu$_3$O$_{7-\delta}$, the main contributions arise from lattice vibrations, weakly interacting paramagnetic centers, and a linear term $C_{\text{lin}} = \gamma(0)T$ of uncertain origin. All three are sample-dependent. In order to separate the $d$-wave contribution of interest, the Stanford \cite{8,9} and Berkeley \cite{10,11} groups fitted models to their data, and concluded that a $d$-wave contribution was present. Numerical results were: $\alpha = 0.10$ to 0.11 mJ/K$^3$mol, $A_c = 0.88$ to 0.91 mJ/K$^2T^{1/2}$mol according to Moler et al., \cite{8,9} who used both twinned and untwinned crystals, and $\alpha = 0.064 \pm 0.02$ mJ/K$^3$mol, $A_c = 0.91$ mJ/K$^2T^{1/2}$mol according to Wright et al., \cite{11} who used ceramic samples. In this paper, we report low temperature specific heat measurements for a twinned and fully oxidized YBa$_2$Cu$_3$O$_7$ crystal in higher fields. The concentration of magnetic impurities for this new crystal is so low that it is possible to see for the first time in YBa$_2$Cu$_3$O$_{7-\delta}$ the contribution due to line nodes in the raw data prior to any correction or fit. Most uncertainties due to the background are avoided by looking at the difference between the specific heat in a magnetic field and that in zero field, $C_{\text{diff}}(B, T) = C(B, T) - C(0, T)$, which is electronic in origin. We obtain $\alpha = 0.21$ mJ/K$^3$mol$\pm 20\%$ and $A_c = 1.34$ mJ/K$^2T^{1/2}$mol$\pm 3\%$. Together with recent results from thermal conductivity, \cite{12} photoemission, \cite{13} and tunneling spectroscopy, \cite{14} these new values allow a numerically consistent picture of the anisotropy of the order parameter for YBa$_2$Cu$_3$O$_7$ to be constructed. A second issue that can be studied
II. EXPERIMENTAL RESULTS

1. Sample

The sample used for the present measurement is a 18 mg YBa$_2$Cu$_3$O$_{7.00}$ single crystal (code AE429G) flux-grown in a BaZrO$_3$ crucible. The latter non-reactive material allows a slow growth with little contamination. Final chemical purity is better than 99.995%. Large crystals have to be screened because of possible CuO/BaCuO$_2$ flux inclusions. The effect of this second phase is potentially huge since only 0.9% BaCuO$_2$ in weight would double the heat capacity of the sample at 3 K, with an intricate field dependence. The present crystal, about $2 \times 1.5 \times 1$ mm$^3$ in size, is twinned, with its smallest dimension along the $c$-axis. Detwinning was not attempted, as it was found that standard procedures used for crystals of that size lead to a degradation of their properties in terms of transition width and concentration of magnetic centers. The sample was fully oxygenated in 100 bar O$_2$, 330C, for 200 hours. The calorimetric transition midpoint, $T_c = 87.8$ K, is typical of overdoped YBa$_2$Cu$_3$O$_{7.00}$. The unextrapolated peak-to-peak amplitude of the $C/T$ anomaly at $T_c$ is 61 mJ/K$^2$mol, i.e. 4.5% of the essentially phononic background (Fig. 1). This amplitude is reproducible for crystals grown in BaZrO$_3$ (cf. 18 mg crystal AE195G and 40 mg crystal AE276G). Fully oxidized samples are preferred for the present purpose for two reasons: clusters of oxygen vacancies effectively act as residual impurities, introducing scattering that could modify drastically the shape of the DOS at $E = 0$ in a $d$-wave superconductor, and a correlation has been observed between the concentration of oxygen vacancies and the amplitude of the Schottky anomaly, which tends to mask the $d$-wave contribution.

2. Specific heat: method and tests.

The low temperature specific heat was measured for $1.2 \leq T < 5$K and $0 \leq B \leq 14$T using a thermal relaxation technique. For calibration purpose, we first measured in $B = 0$
two silver samples of 6N purity with masses 9 and 21 mg. This allowed us to determine independently the heat capacity of the addenda (sapphire sample holder, contributing part of the phosphor bronze suspension wires, epoxy, carbon film heater/thermometer, silicone grease for sample mounting) and the specific heat of silver, which could be then compared with reference data. The heat capacity of the smaller Ag sample was on the same order of magnitude as that of the YBa$_2$Cu$_3$O$_7$ crystal in the middle of the temperature range. We verified that the measured specific heat of Ag after subtraction of the addenda did not change significantly with the field. Silver, which has a small nuclear magnetic moment, presents over copper standards the advantage of a negligible nuclear heat capacity in the temperature and field range investigated here. Figure 2 shows the measured low temperature specific heat of silver, together with reference data. [24] The insert of Fig. 2 shows the Sommerfeld constant γ and Debye temperature Θ$_D$ obtained in fields $B = 0, 4, 8$ and $14$ T. The results are consistent with accepted values Θ$_D = 226$ K and $γ = 0.65$ mJ/K$^2$mol. [24] Note that for YBa$_2$Cu$_3$O$_7$, the Debye specific heat $C \propto Θ^{-3}_D$ is 6.7 times smaller (per gram-atom), so that the determination of $γ(B)$ is more accurate.

Specific heat data can be measured both with increasing and with decreasing temperature. The former are obtained from the response to switching on the heater, the latter to switching off. The heat capacity is given in both cases by:

$$[R(T(t)) - R(T(∞))]I^2 = C(T(t)) \frac{dT}{dt} + \int_{T(∞)}^{T(t)} k(T')dT'$$  \hspace{1cm} (1)

where $R(T)$ is the resistance of the carbon film used both as a heater and a thermometer, $I$ is the current through the film, set to a constant value at time $t > 0$, $C(T)$ is the total heat capacity at temperature $T$, $T(∞)$ is the final asymptotic temperature for a given value of $I$ (measured typically after ten time constants), $k(T)$ is the thermal conductivity of the supporting wires, measured separately when $dT/dt = 0$ using various heater powers and various base temperatures. We use the approximations $T(t) = (T_n + T_{n+1})/2$ and $dT/dt = (T_{n+1} - T_n)/(t_{n+1} - t_n)$ with 50 ms time intervals between the $n^{th}$ and $(n+1)^{th}$ data acquisition, therefore a single relaxation provides numerous independent $C(T)$ points. These
data tend to accumulate at the end of a relaxation until the error on \((dT/dt)^{-1}\) diverges; we discard data with \(|T_{n+1} - T_n| < 4\ mK\). Such accumulations are seen in Fig. 2 and Fig. 4 near \(T^2 = 2, 5, 11\) and 22 K. The up/down procedure allows one to check that measurements are independent of the heating rate (i.e., there is no "\(\tau_2\) effect" in the sense of Ref. [25]). On a fine scale, there is a time dependence of the specific heat of \(\text{YBa}_2\text{Cu}_3\text{O}_7\) at the highest fields and lowest temperatures. This is due to the hyperfine specific heat of Cu nuclei, which are weakly coupled to the electrons [27]. Data at \(T < 1.5\ K\) in \(B = 14\ T\) are discarded for this reason.

3. Specific heat of the \(\text{YBa}_2\text{Cu}_3\text{O}_7\) crystal.

Figure 4 shows the low temperature specific heat of sample AE429G in different magnetic fields, shown separately for \(B||[001]\) along the c-axis (Fig. 4a), for \(B||[110]\) along the ab-diagonal where a gap node is expected (Fig. 4b), and for \(B\) along both the a- and b-axes (the sample is twinned), i.e. along the antinodal direction (Fig. 4c). For the sake of simplicity, the latter direction is called \(B||[100]\). These are raw data, i.e. only the heat capacity of the sample holder is subtracted, otherwise no correction is performed for possible \(\text{BaCuO}_2/\text{CuO}\) impurities originating from flux, [18] paramagnetic centers with \(S = 1/2\) and/or \(S = 2\), [20] nuclear hyperfine contribution, [27] etc. In a first approximation the specific heat is essentially the sum of two dominant contributions. The \(C_{\text{ph}} \approx \beta T^3\) lattice term shows up as a field-independent slope in the \(C/T\) versus \(T^2\) plot, whereas the field-dependent electronic term \(C_{\text{el}} \approx \gamma(B)T\) shifts the curves parallel to each other.

The Schottky effect of residual paramagnetic centers causes a low-temperature upturn in low fields, and a characteristic maximum of \(C_{\text{Sch}}/T\) at \(T_{\text{max}}[\text{K}] = 0.415B[\text{T}]\) for \(S = 1/2\) spins. At high fields, the amplitude of the maximum decreases whereas its width increases, so that the Schottky contribution finally merges into the background. By fitting the expression

\[
C_{\text{sch}} = \frac{Nz^2e^z}{(e^z + 1)^2}, \quad z = \frac{2gS\mu_BB_{\text{eff}}}{k_BT}, \quad B_{\text{eff}} = \sqrt{B_{\text{ext}}^2 + B_{\text{int}}^2}
\]

we find \(N = 0.12\pm 0.02\ \text{mJ/K.gat}\), i.e. 0.005 to 0.007% spins-1/2 per Cu atom, and \(gS = 1.1\) to 1.15 [28]. The amplitude \(N\) and the value of \(gS\) are determined for \(B = 4\) or 8 T along the
in order to minimize the relative vortex contribution and to locate the maximum of the Schottky peak in a convenient temperature range. In this fit, which only serves to characterize the Schottky contribution, we have assumed that the other terms are $\beta T^3$ for phonons and $\gamma(B)T$ for electrons (a more general analysis is given in Section 3). Imposing then the same value of $N$ for $B = 0$ or 0.5 T, we obtain an equivalent interaction field $B_{\text{int}} \approx 0.2$ to 0.5 T. The Schottky term is small relative to the vortex term for $B \parallel c$, but is significant for $B \perp c$ at intermediate fields. In particular, it explains why the raw data at 14 T do not lie clearly above those in 8 T in Fig. 4b and Fig. 4c, in spite of the monotonically increasing vortex term. In any case, high fields improve the ratio of the vortex specific heat over the Schottky specific heat.

Extrinsic magnetic contributions for sample AE429G are unusually small. This is not an artifact. Measurements performed in our laboratory on other samples, including ceramics and detwinned single crystals from various sources have shown a more usual typical concentration of $\approx 0.1\%$ spin-1/2 centers per copper atom. Such "impurities" make it difficult to separate all contributions, in particular at low fields where magnetic interactions between spins cannot be neglected.

The present measurements are compared with earlier work on YBa$_2$Cu$_3$O$_{7-\delta}$ single crystal in Fig. 3. The same fields and the same presentation as for Fig. 3 of Ref. 8 are used, i.e. a $\beta T^3$ term is subtracted. The present data differ in the following respects: the measurement range is shifted by a factor of roughly two toward low temperature where the phonon contribution is smaller; the $\beta$ coefficient is $\sim 20\%$ smaller (possibly owing to hardening of Cu-O chain at full oxygenation, but also to a smaller high-order electronic contribution); the magnetic Schottky term causing deviations from a horizontal line in non-zero field is suppressed by a factor of 15; the residual linear term $\gamma(0)$ is $\sim 30\%$ smaller (but similar to that of sample U1 in Ref. 9). These features, which can be summarized by saying that all non-$d$-wave terms contribute less, facilitate the analysis and give more weight to the $d$-wave specific heat for the present crystal.
III. DISCUSSION

1. Field along the $c$-axis.

In order to get a preliminary insight into the final results, we plot again the data of Fig.4(a) $(B\parallel c)$ in Fig.4(d), after having subtracted the 8 Tesla curve taken as a reference. The remaining specific heat qualitatively shows the evolution of the field-dependent electronic contribution $C_e/T$. Anticipating the discussion, we expect the high field curves to be free of the anomalous $C \propto T^2$ term, hence the choice of the 8 Tesla curve as a reference. Higher fields would only introduce more scatter. This plot only involves smoothing of the reference curve (residuals are shown by the 8 T data set), but neither parameter fit nor correction of any kind. Fig.4(d) evidences the parallel shift of the curves in high fields, $C_e/T = f(B)$, and the progressive appearance of a positive slope at very low fields, ending into a $C_e/T \propto T$ term in $B = 0$. The small upturn at low temperature in the low field curves, together with the faint maximum barely observable at intermediate fields, can be both explained by the presence of a small residual Schottky contribution. At the highest fields and lowest temperatures, data obtained from separate relaxations at different velocities $dT/dt$ do not join smoothly because of the weak coupling of electrons with Cu nuclei. 

The analysis of a difference $C(T, B) - C(T, B_{ref})$ circumvents the problem of modeling the field-independent background (lattice specific heat, residual ”linear term”, etc.). However, in the present status of knowledge a field-independent sub-linear or logarithmic term is no more justified than a linear one, so that we avoid any fit of the background. The following discussion will only depend on differences. However, for a comparison with theory, $B_{ref} = 0$ is more convenient as a reference than $B_{ref} = 8$ T. Therefore we shall concentrate on $C_{dif}(T, B) = C(T, B) - C(T, 0)$.

Figure 5 shows $C_{dif}(B)$ at fixed temperatures $T = 2, 3, \text{and } 4$ K, prior to correction for the magnetic Schottky effect. It is immediately apparent that the vortex specific heat increases approximately with the square root of the field. This behavior can be readily
explained by existing theory, up to the deviations from the square root law. We briefly recall the essential results.

Volovik et al. [3,29,30] first pointed out that in the mixed state of a superconductor with line nodes, supercurrents around a vortex core cause a Doppler shift of the quasiparticle excitation spectrum. If the superfluid velocity is $\vec{v}_s$, the quasiparticle excitation spectrum $E(\vec{k})$ is shifted by $\vec{k} \cdot \vec{v}_s$. This shift has important effects around nodes, where its value is comparable to the width of the superconducting gap. The density of states at the Fermi level is strongly affected:

$$N(0) = n \int \frac{d^3k}{(2\pi)^3} \int d^2r \delta(E(\vec{k}, \vec{r}) - \vec{k} \cdot \vec{v}_s(\vec{r}))$$ (3)

The average superfluid velocity depends on the inverse intervortex distance, $\langle v_s \rangle \propto 1/R(B)$, so that the integral is proportional to $R(B) \propto 1/B^{1/2}$. For $B \gg B_{c1}$, the number of vortices $n$ is proportional to $B$, so that $N(0) \propto B^{1/2}$ and $C_{el}/T \propto B^{1/2}$ at $T \to 0$. Thus one has two regimes, depending on whether the thermal energy $k_B T$ is large or small compared to the typical Doppler energy, one that is quadratic in $T$ ($C_{el} = \alpha T^2$) in zero field at $T \ll T_c$, and one that is linear in $T$ ($C_{el} = A_c B^{1/2}$) at zero temperature and $B \ll B_{c2}$. More precisely, for a weak-coupling superconductor with $d_{x^2-y^2}$ symmetry, Kübert et al. [31] and Vekhter et al. [15,32] obtained:

$$\frac{C_{el, [001]}}{\gamma_n T} = \frac{8}{\pi} \frac{B}{B_{c2}/a^2}^{1/2} + \frac{14}{15} \frac{(2\pi)^{1/2}}{\Delta_0^2} \frac{(2\pi)^{1/2}}{B} \frac{(B_{c2}/a^2)}{B}$$ (4)

$$\frac{C_{el, [001]}}{\gamma_n T} = \frac{27\zeta(3)}{\pi^2} \frac{k_B T}{\Delta_0} + \frac{3 l \ln 2}{2\pi} \frac{\Delta_0}{k_B T} \frac{B}{B_{c2}/a^2} + \ldots$$ (5)

where $\zeta(3) = 1.202...$ and $a$ is a constant of order unity depending only on the vortex lattice geometry. The latter constant is defined differently in Ref. [31] and [15,32]; we have chosen here the notation of Refs. [12] and [31] (see note [33]). These equations may be rewritten in terms of the Fermi velocity $v_F$ to avoid any reference to the ill-defined upper critical field of HTS. In this form, they are no longer restricted to the weak-coupling case. Keeping only the leading terms, we have then:
\[
\frac{C_{el,[001]}}{\gamma_n T} = \frac{4a}{\Phi_{0/2}^1} \frac{\hbar v_F}{\pi \Delta_0} B^{1/2} + \ldots, \quad \frac{\Phi_{0/2}^1 k_B}{\hbar v_F} \frac{T}{B^{1/2}} \ll 1
\]  

(6)

\[
\frac{C_{el,[001]}}{\gamma_n T} = \frac{27\zeta(3)}{\pi^2} \frac{k_B}{\Delta_0} T + \ldots, \quad \frac{\Phi_{0/2}^1 k_B}{\hbar v_F} \frac{T}{B^{1/2}} \gg 1
\]  

(7)

These asymptotic formulas extrapolate to the same result at a crossover temperature \(T_{\text{cross}}(B)\) given by:

\[
T_{\text{cross}}(B) = \left(\frac{2\pi}{27\zeta(3)}\right)^{3/2} \frac{\Delta_0}{k_B} \left(\frac{B}{B_{c2}/a^2}\right)^{1/2}
\]  

(8)

The ratio between the experimental parameters \(A_c\) and \(\alpha\) depends only on the Fermi velocity:

\[
\frac{A_c}{\alpha} \equiv \frac{\lim_{T \to 0} (C/T B^{1/2})}{\lim_{B \to 0} (C/T^2)} = \frac{T_{\text{cross}}(B)}{B^{1/2}} = \frac{4\pi \hbar}{27\zeta(3)\Phi_{0/2}^1 k_B} \alpha v_F
\]  

(9)

The full function across the crossover regime has not been calculated analytically, but has the following scaling property: \[33\text{-}34\]

\[
\frac{C_{el,[001]}}{\gamma_n T} \left(\frac{B_{c2}}{B}\right)^{1/2} = F_{c,[001]}(x)
\]  

(10)

where \(x \equiv T/T_{\text{cross}}(B)\). \[33\] The empirical interpolating function

\[
F_{c,[001]}(x) \approx \left(\frac{8}{\pi}\right)^{1/2} a(1 + x^2)^{1/2}
\]  

(11)

allows one to map the full specific heat function (Fig. 6). Far above the crossover temperature, the Doppler shift can be neglected, so that only the bulk term \(C/T \propto T\) arising from the V-shape of the DOS survives. Conversely, far below \(T_{\text{cross}}(B)\), only the field-dependent plateau in the DOS at \(E \to 0\) is probed by thermal excitations, so that the Doppler term \(C/T \propto B^{1/2}\) dominates. In any case one has assumed \(T \ll T_c\) and \(B \ll B_{c2}\), which is satisfied in the present data limited to \(T < 5\) K and \(B \leq 14\) T. As we shall see below, \(T_{\text{cross}}/B^{1/2} \approx 6.4\) K/T\(^{1/2}\) when \(B \parallel c\), so that measurements of \(C_{\text{diff}}(T, B)\) from 2 to 4 K in fields from 0.16 to 14 T probe the region \(0.085 \leq x \leq 1.6\), which spans both the high field/low temperature limit and the crossover regime \(x \approx 1\). This implies that both constants \(A_c\) and \(\alpha\) can be determined independently from the data.
Since we are interested in the difference $C_{\text{dif}}$, the relevant scaling function is $F_{\text{dif}}(x)$ defined by:

$$
\frac{C_{\text{dif},[001]}}{\gamma_n T} = \left( \frac{B}{B_{c2}} \right)^{1/2} F_{c,[001]}(x) - \frac{27\zeta(3)k_B}{\pi^2\Delta_0} T \equiv \left( \frac{B}{B_{c2}} \right)^{1/2} F_{\text{dif},[001]}(x) \quad (12)
$$

and the corresponding interpolation function becomes:

$$
F_{\text{dif},[001]}(x) \simeq \left( \frac{8}{\pi} \right)^{1/2} a\left[ (1 + x^2)^{1/2} - x \right] \quad (13)
$$

Figure 7 shows the scaling plot $C_{\text{dif}}/TB^{1/2}$ versus $T/B^{1/2}$ corresponding to Eq.(12). The data for $B||c$, measured at fixed temperatures $T = 2, 3$ and $4$ K, and now corrected for the Schottky contribution (in the main frame, not in the insert), collapse onto a single curve, thus supporting the existence of line nodes. This test also shows that the additional energy scale introduced by possible impurity scattering is negligible compared to the other scales determined by thermal smearing and Doppler shift. Strong impurity scattering would lead to a breakdown of the scaling property, with $N(0)$ decreasing ultimately as $|B\log B|$ rather than $B^{1/2}$ at low fields. A comparison with numerical calculations (Fig. 4 of Ref. [31]) shows that our data lie essentially in the clean limit. This also implies that the observed residual linear term $\gamma(0)T$, with $\gamma(0) \approx 15\%$ of the normal-state Sommerfeld constant $\gamma_n$, is mostly not caused by impurity scattering.

Figure 8 shows how parameters $A_c$ and $\alpha$ can be extracted directly from the data. We plot $C_{\text{dif}}/T$ versus $B^{1/2}$ at $T = 2, 3$ and $4$K. At high fields, data fall on parallel lines. This is the region $x \ll 1$ where

$$
\left. \frac{C_{\text{dif},[001]}}{T} \right|_{x \ll 1} \simeq 1.596 a\frac{\gamma_n B^{1/2}}{B_{c2}^{1/2}} - 3.288 \frac{\gamma_n k_B}{\Delta_0} T \equiv A_c B^{1/2} - \alpha T \quad (14)
$$

The slope determines the leading field-dependent term with $A_c = 1.34$ mJ/K$^2$T$^{1/2}$mol $\pm$ 3%, whereas the parallel shift with changing temperature in the high field limit determines the bulk term with $\alpha = 0.21$ mJ/K$^3$mol $\pm$ 20%. Their ratio yields $a v_F \simeq 1.0 \times 10^7$ cm/s. Together with the maximum gap width $\Delta_0 = 20$ meV determined by scanning tunneling spectroscopy, we further obtain $\gamma_n \simeq 15$ mJ/K$^2$mol and $B_{c2}/a^2 \simeq 310$ T. These results agree
with the re-evaluation by Kübert and Hirschfeld of earlier data characterized by various scattering rates. [31] The crossover temperature is given by \( T_{\text{cross}}/B_1^{1/2} = A_c/\alpha = 6.4 \text{ K}/T^{1/2} \). The parameters \( A_c \) and \( \alpha \) are substantially larger than those determined earlier and recalled in the Introduction. This may be due in part to the use of a crystal that is overdoped rather than optimally doped. Scattering by impurities is probably lower. [31] In addition, the methods used by different authors have different sensitivities to various sources of experimental errors. The present results allow one to construct a scenario in the framework of \( d_{x^2-y^2} \) pairing symmetry that is consistent with other types of experiments such as tunneling spectroscopy and thermal conductivity. Following Chiao et al. [12] we assume a cylindrical Fermi surface; the \( A_c \) parameter can be expressed in terms of the slope \( v_2 \equiv \partial \Delta/\partial p_\perp \) of the gap on the Fermi surface in the direction perpendicular to the line of nodes:

\[
A_c = \frac{8k_B^2}{3\hbar \Phi_0^{1/2}} \frac{V_{\text{mol}} a}{d} \frac{1}{v_2} \tag{15}
\]

This follows from Eq. 6 with \( \gamma_n = (\pi^2/3)k_B^2 N(0)V_{\text{mol}}, N(0) = m^*/(\pi\hbar^2 d) \) where \( d = c/2 = 0.584 \text{ nm} \) is the average interlayer distance, \( V_{\text{mol}} = 104.6 \text{ cm}^3/\text{mol} \) the molar volume, \( \Delta(\phi) = \Delta_0 \cos(2\phi) \), and \( |d\Delta(\phi)/d\phi|_{\phi=\pi/4} = \hbar k_F v_2 = 2\Delta_0 \) at the node. Eq. (15) yields \( v_2/a \approx 1.4 \times 10^6 \text{ cm/s} \). In the same approximation, \( \alpha \) is given by

\[
\alpha = \frac{18\zeta(3)k_B^3}{\pi\hbar^2} \frac{V_{\text{mol}}}{d} \frac{1}{v_2 v_F} \tag{16}
\]

which yields \( v_2 v_F \approx 1.4 \times 10^{13} \text{ (cm/s)}^2 \). Up to this point, the geometrical parameter \( a \) is undetermined. The recent analysis of thermal conductivity in the universal low temperature regime by Chiao et al. [12] determined \( v_F/v_2 = 14 \pm 20\% \) in \( \text{YBa}_2\text{Cu}_3\text{O}_7 \). Combining this result with ours one obtains \( v_F \approx 1.4 \times 10^7 \text{ cm/s}, v_2 \approx 1.0 \times 10^6 \text{ cm/s}, a \approx 0.70, B_{c2} \approx 150 \text{ T} \), corresponding to a coherence length \( \xi \approx 15 \text{ Å} \). The geometrical parameter is of order one as anticipated, and the upper critical field is consistent with previous estimations. [35,36]

The Fermi velocity is smaller than determinations based on angle-resolved photoemission spectroscopy (ARPES), \( v_F \approx 2.5 \times 10^7 \text{ cm/s} \). [13] The difference appears to be real, even taking into account the large uncertainty margin on this parameter (Table I), and may be
due to a contribution from chain states with a low Fermi velocity in our overdoped sample. In this respect it is interesting to note that YBa$_2$Cu$_4$O$_8$, which contains completely filled double chains, presents a large negative curvature in the plot of $C/T$ versus $T^2$ in $B = 0$ at $T < 5$ K. If this curvature is attributed to a bulk $d$-wave $\alpha T^2$ term, then $\alpha$ is still three times larger (per chain) for YBa$_2$Cu$_4$O$_8$ than for YBa$_2$Cu$_3$O$_7$, and consequently the product $v_2 v_F$ is three times smaller, showing a potential source of variations of $v_F$. The Fermi wave number is $k_F = 2\Delta_0/hv_2 \cong 0.6 \overset{\text{A}}{=} 3/4 \pi/a_1$ ($a_1 \cong 3.85 \overset{\text{A}}{=} 0$ is the lattice constant). The latter result is consistent with the quasi-2D hole band centered on the S-point ($\vec{k} = [\pi/a_1, \pi/b, 0]$) found by band structure calculations and by ARPES, which show that plane states cross the Fermi surface near $k_F \cong 0.69$ to $0.75 \overset{\text{A}}{=} 0$ along the nodal direction and $k_F \cong 0.58$ to $0.64 \overset{\text{A}}{=} 0$ along the antinodal directions. The overall consistency provides strong support to the quasi-2D, $d_{x^2-y^2}$-wave model. In particular using a normalized gap function $\Delta(\phi)/\Delta_0$ similar to that of Bi$_2$Sr$_2$CaCu$_2$O$_8$ does not lead to any contradiction.

Based on the previous data, one can further evaluate the Fermi temperature $T_F = \hbar k_F v_F/2k_B = (\Delta_0/k_B)(v_F/v_2) \cong 3300$ K and the mass enhancement factor $m^*/m_e = \hbar k_F/m_e v_F \cong 5$. Note that the latter ratio depends only on the product of experimental quantities $\Delta_0 \alpha$. It is interesting to note that the Bose-Einstein condensation temperature of such heavy quasi-2D hole pairs, if preformed above $T_c$, should occur at

$$T_{BE} = \frac{2\pi \hbar^2 n d}{k_B m^* \ln(\frac{1}{\hbar \xi^2 m^* d^2})} \cong 100$ K (17)$$

where $\Gamma = 5.3$ is the anisotropy ratio of the upper critical field. For the pair density, we used the value $n = 1.0 \times 10^{21} cm^3$ obtained by scaling the amplitude of the $\lambda$ anomaly of the specific heat of $^4$He at 2.18 K, for which the boson density is $n_b = 2.2 \times 10^{22} cm^3$, to the $\lambda$-anomaly of YBa$_2$Cu$_3$O$_7$ at $T_c$. The fact that $T_{BE}$ is close to $T_c$ may be a coincidence for YBa$_2$Cu$_3$O$_7$, since the penetration depth calculated from these parameters exceeds experimental values by a factor of about two. Additionally, the ratio $\Delta_0/E_F = 2/(\pi k_F \xi) \cong (v_2/v_F) \cong 1/14$ shows that only a small part of the carriers near the
Fermi surface are paired.

Finally the initial assumption that vortex core levels do not contribute significantly to the specific heat at low temperature can be tested \textit{a posteriori}. Self-consistent calculations of the electronic structure of a vortex line in NbSe$_2$ have shown that the lowest energy excitation depends on temperature, with a value at $T \ll T_c$ of the order of $E_{1/2} \simeq \Delta_0^2/E_F$.\[[41]\] Applying the same criterion to YBa$_2$Cu$_3$O$_7$ leads to $E_{1/2}/k_B \simeq 17$ K, about half the estimation based on STS,\[7\] but large enough to be neglected in the specific heat below 4 K.

The above determinations are summarized in Table I. In order to evaluate uncertainty margins, we included the error on experimental parameters $A_c$, $\alpha$, and $v_F/v_L$, and neglected that on $\Delta_0$.

2. $B \parallel ab$-plane

The main motivation of the measurements for $B \perp c$ was the prediction of a variation of $\gamma(T = 0, B, \phi)$ with the azimuthal angle $\phi$ between the field and the $a$-axis.\[[15]\] The qualitative physics underlying this effect may be understood by noticing that when a field is applied along the antinodal [100] direction, all four nodes contribute equally to the DOS, with an amplitude proportional to $4 \cos(\pi/4)$, whereas for $B$ along the nodal direction [110], the Doppler effect vanishes for those particles which travel parallel to the field, so that only two nodes contribute with an amplitude proportional to $2 \cos(0)$. Quantitative estimations depend on details of the theory, so that a 30% variation appears as an upper limit for a clean, tetragonal crystal with a 2D band. Such fourfold oscillations of $\gamma(T = 0, B, \phi)$ versus $\phi$, if observed, would provide a robust test of $d$-wave symmetry. Moler et al.\[9\] did not observe any such oscillation within experimental resolution. A second motivation is the experimental verification of the general features of the vortex specific heat predicted theoretically for $B \perp c$\[[15,32]\].

Data analysis for $B \perp c$ is more involved than for $B \parallel c$ (compare Fig. 9 and Fig. 5). Even for the present crystal, the residual Schottky contribution due to paramagnetic centers is no longer negligible compared to the reduced vortex contribution. We face for the $B \perp c$
configuration the same problem as the Stanford \[8,9\] and Berkeley \[10,11\] groups did for the \(B∥c\) configuration. As data for \(B⊥c\) are expected to lie in the crossover regime (the crossover temperature scales with \((B/\Gamma)^{1/2}\)), a fit to a \(C = A_{ab}TB^{1/2}\) law is not justified beforehand. We resort then to a scaling plot which is more generally valid, first using raw data (Fig. 10a; note that the scaling variable is \(B^{1/2}/T\) in this plot, so that unlike Fig. 7 high fields are on the right). At this stage, data do not collapse on a common curve. In the same figure we plot the Schottky specific heat of spin-1/2 paramagnetic centers, with a concentration equivalent to 0.006% of the Cu atoms. The position of the peaks corresponds to the maxima of the raw data, confirming that the paramagnetic centers have a spin \(S = 1/2\). Note that the Schottky correction is negligible in \(B = 14\ T\). In the scaling plot of Fig. 10b, we show the data after having subtracted the Schottky contribution. The parameters of the Schottky anomaly were adjusted manually to obtain the best collapse onto a common curve. In this operation, the most efficient parameter is the concentration of paramagnetic centers; only minor improvements are obtained by refining the gyromagnetic ratio and the interaction field. Data define a wide high field region \((T/B^{1/2} < 2\ K/T^{1/2})\) where \(C = A_{ab}TB^{1/2}\), \(A_{ab} = 0.18\ mJ/K^2T^{1/2}\)mol \(±10\%\), therefore \(A_c/A_{ab} \approx 7.4\). The latter determination does not depend critically on the subtraction of the Schottky anomaly; it suffices to consider only 14 T data, \(B⊥c\), where the Schottky contribution can be neglected, and compare with 14 T data, \(B∥c\) (Fig. 9 and Fig. 5).

The ratio \(A_c/A_{ab}\) is larger than the square root of the anisotropy ratio at \(T_c, \Gamma^{1/2} = 2.30 \pm 0.07\). This is expected, at least qualitatively. We recall the results of Ref. \[15,32\] for the specific heat with the field parallel to the planes, assuming moderate anisotropy, cylindrical Fermi surface and \(\Delta_k = \Delta_0 \cos(2\phi)\):

\[
\frac{C_{el}}{\gamma_nT} = \frac{2}{\pi} \left( \frac{B/\Gamma}{B_{c2}/a^2} \right)^{1/2} + \frac{27\zeta(3)k_B T}{2\pi^2} \frac{k_B T}{\Delta_0} + \ldots, B∥[[110]], \frac{T(B_{c2})^{1/2}}{T_c B^{1/2}} \ll 1
\]

(18)

\[
\frac{C_{el}}{\gamma_nT} = \frac{2}{\pi^{1/2}} \left( \frac{B/\Gamma}{B_{c2}/a^2} \right)^{1/2} + \frac{28\pi^{1/2}}{15} \left( \frac{k_B T}{\Delta_0} \right)^2 \left( \frac{B_{c2}/a^2}{B/\Gamma} \right)^{1/2} + \ldots, B∥[[100]], \frac{T(B_{c2})^{1/2}}{T_c B^{1/2}} \ll 1
\]

(19)

\[
\frac{C_{el}}{\gamma_nT} = \frac{27\zeta(3)k_B T}{\pi^2} \frac{k_B T}{\Delta_0} + \frac{3\ln 2}{4\pi} \frac{\Delta_0}{k_B T B_{c2}/a^2} + \ldots, B∥[[110]], B∥[[100]], \frac{T(B_{c2})^{1/2}}{T_c B^{1/2}} \gg 1
\]

(20)
As before, we have restored the convention for the geometrical parameter $a$ of Ref. [31]; see Note [33]. In the high temperature regime, one recovers the bulk isotropic $C \propto T^2$ behavior, irrespective of the field direction. At $T = 0$, the expected ratio between the $c$-axis and nodal specific heat is $C(0, B||[001])/C(0, B||[110]) = 2\Gamma^{1/2} \approx 4.6$, that between the $c$-axis and antinodal specific heat is $C(0, B||[001])/C(0, B||[100]) = (2/\Gamma)^{1/2} \approx 3.3$. The theoretical parameter-free curves given by the second-order approximations, Eq. [18-20], are plotted in Fig. 10b. The order of magnitude is correct, but Eq. [18-20] first fail to reproduce the wide plateau for $B^{1/2}/T > 0.5 \text{T}^{1/2}/\text{K}$, second tend to overestimate the vortex specific heat for large values of $B^{1/2}/T$, and third predict an in-plane anisotropy for large values of $B^{1/2}/T$ that is not observed. There is no way to improve the agreement by changing the spin and the amplitude of the Schottky correction, which is negligible for large values of $B/T$.

One is tempted to conclude that the anisotropy ratio at low temperature is larger than the value $\Gamma = 5.3$ found at $T_c$ (an example of such behavior is given by $2\text{H-NbSe}_2$ for which $(B_{c2,n}/B_{c2,c}) = 3.4$ at $T \to 0$ whereas $(dB_{c2,n}/dT)/(dB_{c2,c}/dT) = 2.7$ at $T_c$), [12] but this does not remedy the situation. A larger anisotropy would indeed decrease the coefficient of the vortex term $A_{ab}$, and therefore would shift down the theoretical curves; however this would leave the coefficient of the bulk term $\alpha$ unchanged and, remembering that the zero field specific heat is subtracted in $C_{\text{dif}}$, this bulk term would cause a positive slope for all values of $B^{1/2}/T$ plotted in Fig. 10b. Therefore, the plateau would not be reproduced.

The experimental points show that the difference between the in-field and the zero-field specific heat contains essentially a small vortex term $A_{ab}TB^{1/2}$ for $T/B^{1/2} < 2 \text{K}/\text{T}^{1/2}$, apparently without any $-\alpha T^2$ contribution from the bulk term. Leaving aside the disturbing scenario $\alpha = 0$, one concludes that the application of a field $B\perp c$ leaves the $\alpha T^2$ term unchanged at low temperature, so that it cancels in $C_{\text{dif}}$. In terms of density of states, a small V-shape dip subsists at $E_F$ in the middle of a field-induced plateau that moves up with $B^{1/2}$. Within this picture, the sharp crossover seen experimentally near $T/B^{1/2} = 2 \text{K}/\text{T}^{1/2}$ corresponds to the edge of the dip, not to $A_{ab}/\alpha \approx 0.86 \text{K}/\text{T}^{1/2}$. Such a fine structure of the DOS could indicate that the anisotropic London theory leading to Eq. [18-20], and which
is valid for moderate anisotropy, does not take into account all aspects of vortex physics for $B \perp c$.

The absence of in-plane anisotropy is a second puzzling feature. It is already apparent in the raw data, Fig. 4b and Fig. 4c, and more precisely seen in the scaling plot of Fig. 10b, where the points for $B$ along the antinodal direction hardly differ from those for $B$ along the nodal direction. In order to perform a more quantitative analysis, we focus on the $B = 14$ T data for two reasons: first the Schottky correction is negligible, and second the vortex contribution follows a simple high field $d$-wave law, as just discussed. By fitting the parameters of a model $C/T = \gamma(B) + \beta T^2$ to the data in $B = 14$ T (Table I), we find

$$\gamma(B||[100]) - \gamma(B||[110]) = 0.04 \pm 0.06 \text{ mJ/K}^2\text{mol.}$$

The residuals show no structure suggesting any missing term. The sign is correct but the amplitude is an order of magnitude smaller than the $d$-wave prediction,

$$A_c B^{1/2}[(2\Gamma)^{-1/2} - (4\Gamma)^{-1/2}] = 0.45 \text{ mJ/K}^2\text{mol at 14 T in the clean limit.}$$

The 8 T data confirm the 14 T result. In order to make this comparison as significant as possible, we took care not to add or remove any addendum mass (in particular the adhesive) when rotating the sample at room temperature. The experimental reproducibility is documented by the data in $B = 0$, which were measured separately in each one of the three sample positions [001], [100] and [110] along the magnet axis (Table I).

In order to reconcile the lack of any significant variation of $\gamma(\phi)$ with the existence of $d$-wave pairing, various arguments may be invoked. First, the 2D model of the DOS may be too crude. Numerical estimations have shown that the amplitude of the oscillations of $\gamma(T = 0, B, \phi)$ with $\phi$ is reduced in the 3D case. Second, the full 30% effect develops only at $T = 0$; distinct crossover effects decrease the in-plane anisotropy at any finite temperature, but this reduction is taken into account in the model curves of Fig. 10b. Third, orthorhombicity shifts the sharp minimum of $\gamma(T = 0, B, \phi = \pi/4)$ slightly off the nodal direction. Together with twinning, this replaces the single minimum by a double dip centered on $\phi = \pi/4$ with reduced depth. Scattering may smooth the oscillations; we believe that this is not the main cause here since scattering would also have led to a breakdown of the $\gamma \propto B^{1/2}$ dependence for $B \parallel c$. Finally, the implications of the in-plane
anisotropy of the penetration depth in YBa$_2$Cu$_3$O$_7$, $\lambda_a > \lambda_b$, [14] were not addressed. In short, YBa$_2$Cu$_3$O$_7$ does not appear to be suitable for a quantitative test of $d$-wave pairing symmetry based on $ab$-plane anisotropy, owing to its orthorhombicity.

IV. CONCLUSION

The low contamination of the present crystal by paramagnetic impurities has allowed to observe directly a field-induced contribution to the specific heat of YBa$_2$Cu$_3$O$_7$ that can be accounted for by the theoretical treatment of a $d$-wave superconductor with a quasi-2D band at the Fermi level. The parameters inferred from this experiment have a typical $\pm 20\%$ accuracy as they depend critically on the value of the bulk $T^2$-term of the zero-field specific heat. Together with the results of tunneling spectroscopy, photoemission and thermal conductivity, these results allow an overdetermined and consistent set of microscopic parameters to be established.

The bulk confirmation of $d$-wave properties provided by specific heat is important, as stressed by previous studies on this subject. However experiment and theory still indicate some unsolved puzzles. First recall that a fully gapped s-wave component, if present, would not give rise to any measurable contribution at $T \ll \Delta_0/k_B$, so that the present experiments cannot provide any information on this topic. It has been pointed out that non-linear variations of $\gamma(B)$ with the field also occur in s-wave superconductors, both from an experimental [12,15,16] and theoretical [17,18] point of view. The present experiments probably cannot distinguish between $C \propto B^{1/2}$ and $C \propto B^{0.41}$ as proposed in Ref. [18]. The expected $ab$-plane anisotropy could not be observed. As the present results leave little hope of obtaining a decisive answer using YBa$_2$Cu$_3$O$_7$ as a working material, tetragonal compounds should rather be investigated, preferably with a Ba-free composition in order to avoid the presence of BaCuO$_2$ impurities. The field dependence of the specific heat for $B \perp c$ remains to be explained in detail. Finally, it has been pointed out that the relatively large local DOS that should be present between the vortex cores in the Doppler model has
not been observed up to now by tunneling spectroscopy in YBa$_2$Cu$_3$O$_7$, notwithstanding several attempts [49]. Therefore, in spite of considerable progress, a full understanding of the mixed state of YBa$_2$Cu$_3$O$_7$ has yet to be reached. Bulk investigations of unconventional pairing in other HTS, if they can be prepared with the same degree of purity, would be most informative.

V. APPENDIX

In a previous article, referred to as BR, [50] we have estimated by a different method the vortex specific heat of another crystal (AE37G), also grown in BaZrO$_3$, with a larger Schottky anomaly corresponding to 0.03% spin-1/2 per Cu atom. The field-independent terms were canceled by considering the anisotropic component $C(B∥c)−C(B⊥c)$ rather than the difference $C(B)−C(0)$. It was assumed that anisotropy enters only through the ratio $B_{c2,ab}/B_{c2,c} = 5.3$, an estimation that now has to be revised. BR obtained $A_c = 1.8$ mJ/K$^2$T$^{1/2}$mol, and, noticing that $[C(B∥c)−C(B⊥c)]/TB^{1/2}$ was not constant, concluded that data were taken in the crossover regime.

Now that the specific heat for $B⊥c$ has been measured separately, we can check these conclusions. The present finding is that the specific heat for $B⊥c$ is much smaller than expected. Rather than $C(B∥c)/C(B⊥c) ∝ (B_{c2,ab}/B_{c2,c})^{1/2} ≈ 2.3$ as used in BR, $C(B∥c)/C(B⊥c) ≈ 7.4$ over a wide field range. Therefore $C(B∥c)−C(B⊥c)$ does not contain $1−\Gamma^{−1/2} = 57\%$ of $C_{\text{vortex}}(B∥c)$, but $1−1/7.4 = 87\%$. Our previous result, based on a measured anisotropic component $A_c−A_{ab}= 1.0$ mJ/K$^2$T$^{1/2}$mol at $T→0$, has to be rescaled to $A_c = 1.2$ mJ/K$^2$T$^{1/2}$mol. The difference with the present result, $A_c = 1.34$ mJ/K$^2$T$^{1/2}$mol, is essentially due to the way data were extrapolated to $T = 0$ in Fig. 3 of BR.

The second point is the crossover temperature that separates the low T, high B regime from the high T, low B regime. In a plot of $[C(B∥c)−C(B⊥c)]/TB^{1/2}$ versus $T/B^{1/2}$, the crossover is the value of $T/B^{1/2}$ at which $[C(B∥c)−C(B⊥c)]/TB^{1/2}$ extrapolates linearly to zero, starting from its initial value at $T/B^{1/2} = 0$ (see e.g. Fig. 7). In view of the smallness of
the vortex contribution for \( B \perp c \), one has approximately \( C(B \parallel c) - C(B \perp c) \approx C(B \parallel c) - C(0) \).

Fig. 2 of BR, redrawn on a linear scale, shows that the crossover estimated in this way is \( A_c / \alpha = 5 \) to \( 7 \) K/\( T^{1/2} \) for \( B \parallel c \), consistent with the result for the present crystal AE429G, \( A_c / \alpha = 6.4 \) K/\( T^{1/2} \). In the high field region \( 0 < T/B^{1/2} \ll A_c / \alpha \), thus below the crossover temperature, \( C(B \parallel c) / T B^{1/2} \) is constant but \( [C(B \parallel c) - C(0)] / T B^{1/2} \) must decrease linearly with \( T/B^{1/2} \), a point that was not made clear in BR.

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After completion of this work, we became aware of recent developments in theory, both in the Doppler (Volovik) approach \[51\] and in self-consistent calculations of the electronic structure of a \( d_{x^2-y^2} \) vortex \[52\]. Although the shape of the envelope is preserved, the density of states at the Fermi level in the latter approach is always zero, on a very fine energy scale, irrespective of the field \[53\-55\]. This is not in contradiction with the present results in the 1-4 K range, which are broadened by thermal smearing.
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The informed experimenter might be puzzled by the missing upturn at the lowest temperatures (< 2K) and highest fields (> 10T). The absence of the Cu nuclear specific heat is due to the short characteristic time of our measurement (0.6-0.8s at 1.2 K and 14 T, $B\parallel c$), to be compared with Korringa’s electron-nucleus thermalization time, $\tau_1 T \sim 1.1$ sK. This causes (only at high field and low temperature) a time dependence of the heat capacity; data at the end of a relaxation when $|dT/dt| \to 0$ lie systematically above those obtained at the beginning of a relaxation when $|dT/dt|$ is large (e.g. 0.2-0.4 K/s near 1.3 K). Generally, for a given temperature, we have data taken at both slow and fast rates. By discarding the former we ensure that the nuclear contribution of Cu is in large part eliminated. The same reasoning holds for alternating current specific heat methods; above a few Hertz, Cu nuclei no longer follow the oscillation of the electronic temperature.

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In the definition of the geometrical parameter $a$, we have used the convention of Kübert and Hirschfeld [31] to facilitate comparison with Ref. [12]. The convention used by Vekhter et al. [13,21] is different and ensures that for $a = 1$ there is one flux quantum per unit cell of the vortex lattice approximated by a circle of radius $R = (\Phi_0/\pi B)^{1/2}$. The equivalence is $a \equiv a_{Kübert} = (\pi^{1/2}/2)a_{Vekhter}$. The Doppler energy scales are $E_{H,Kübert} = a\Delta_0(B/B_c)^{1/2}$ in Kübert’s convention and $E_{H,Vekhter} = (a_{Vekhter}\hbar v_F/2)(\pi B/\Phi_0)^{1/2}$ in Vekhter’s convention, so that $E_{H,Kübert} = (2/\pi)^{1/2}E_{H,Vekhter}$. The crossover temperature
at which the high field leading term of the specific heat \( C = AT B^{1/2} \) becomes equal to the bulk term \( C = \alpha T^2 \) corresponds to \( k_B T / E_{H,\text{Kübert}} = 0.485 \), to \( k_B T / E_{H,\text{Vekhter}} = 0.387 \), and to \( x = [27 \zeta(3)/(2\pi)^{3/2}]k_B T / E_{H,\text{Kübert}} = [27 \zeta(3)/(4\pi)]k_B T / E_{H,\text{Vekhter}} = 1 \) in the present work. Of course, physical results do not depend on these conventions.

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FIGURES

FIG. 1. Total specific heat of the present crystal (AE429G) and another crystal also grown in BaZrO$_3$ (AE195G) near $T_c$. The critical temperature is defined here as the point with the largest negative slope of $C/T$ versus $T$.

FIG. 2. Specific heat $C/T$ versus $T^2$ of the silver test sample. Full line: standard reference data. Insert: fitted Debye temperature and Sommerfeld constant in different magnetic fields.

FIG. 3. Comparison of the present data (series (b) on the left side 1.2 - 2.4K). As for Fig. 4 of Ref. 8, the specific heat is plotted per mol units as $(C - \beta T^3)/T$ vs $T$, $\beta = 0.392$ mJ/molK$^2$ for the data of Ref. 8, and $\beta = 0.305$ mJ/molK$^2$ for the present work. The magnetic field is applied perpendicular to the planes. The same subset of fields is shown.

FIG. 4. Low temperature specific heat $C/T$ of YBa$_2$Cu$_3$O$_7$ (AE429G) for different fields, raw data. (a), $B||[001]$, from bottom to top $B = 0, 0.16, 0.5, 1, 2, 3, 4, 6, 8, 10, 12, 14$ T. (b), $B||[110]$, $B = 0, 0.5, 1, 2, 4, 8, 14$ T. (c), $B||[100]$ and [010], $B = 0, 8, 14$ T. (d), same data as (a), after subtraction of the $B = 8$T curve.

FIG. 5. Specific heat $C/T$ versus the field $B$ ($B||c$) at fixed temperatures, raw data, showing a nearly square-root law.

FIG. 6. Model calculation of the low temperature specific heat versus temperature and field ($B||c$) in the presence of line of nodes, showing the high-field, low temperature regions where $C/T \propto B^{1/2}$ and the high temperature, low field regions where $C/T \propto T$. The parameters correspond to those for the present crystal AE429G.

FIG. 7. d-wave scaling plot of the specific heat difference $C_{\text{dif}}/TB^{1/2}$ versus $T/B^{1/2}$ ($B||c$). A Schottky contribution has been subtracted. Full line: interpolated scaling function. Insert: the same plot without correction for the Schottky contribution.
FIG. 8. Plot of the specific heat difference $C_{\text{dif}}/T$ versus $B^{1/2}$ ($B \parallel c$) at fixed temperatures, allowing one to extract the parameters $A_c$ and $\alpha$. A Schottky contribution has been subtracted. Full lines: interpolated scaling function. Insert: the same plot without correction for the Schottky contribution.

FIG. 9. Plot of the specific heat difference $C_{\text{dif}}/T$ versus $B$ ($B \parallel [110]$) at fixed temperatures, raw data.

FIG. 10. (a), same raw data as for Fig. 9 ($B \parallel [110]$) in a scaling plot $C_{\text{dif}}/TB^{1/2}$ versus $B^{1/2}/T$. The full lines show the estimated Schottky contribution at different temperatures. (b), remaining vortex contribution after having removed the Schottky anomaly, both for $B \parallel [110]$ and $B \parallel [100]$ Dotted and dashed lines: anisotropic $d$-wave model (see text).
$$V_{\text{mol}} = 13V_{\text{gat}}$$

$$M_{\text{mol}} = 13M_{\text{gat}}$$

$$T_c = 87.8 \pm 0.05 \text{ K}$$

$$\Gamma = 5.3 \pm 0.3$$

$$A_c = 1.34 \pm 3 \%$$

$$A_{ab} = 0.18 \pm 10 \%$$

$$\alpha = 0.21 \pm 20 \%$$

$$v_2/a = 1.42 \times 10^6 \pm 3 \%$$

$$v_F v_2 = 1.4 \times 10^{13} \pm 20 \%$$

$$a v_F = 1.0 \times 10^7 \pm 24 \%$$

$$a^2 v_F / v_2 = 6.9 \pm 27 \%$$

$$T_{\text{crossover}} / B^{1/2} = 6.4 \pm 24 \%$$

$$\Delta_0 = 20 \text{ meV}$$

$$\gamma_n = 15 \pm 20 \%$$

$$B_{c2} / a^2 = 310 \pm 11 \%$$

$$m^*/m_e = 5.1 \pm 20 \%$$

$$v_F / v_2 = 14 \pm 20 \%$$

$$a = 0.70 \pm 23 \%$$

$$v_F = 1.4 \times 10^7 \pm 53 \%$$

$$v_2 = 1.0 \times 10^6 \pm 27 \%$$

$$B_{c2} = 150 \pm 68 \%$$

$$\xi = 15 \pm 30 \%$$

$$k_F = 0.61 \pm 27 \%$$

$$T_F = 3300 \pm 20 \%$$
TABLE I. YBa$_2$Cu$_3$O$_{7}$ parameters obtained from the field-induced specific heat. Rows below $\Delta_0$ make use of the gap value from tunneling spectroscopy. Rows below $v_F/v_2$ make use of this ratio from thermal conductivity. See text for definitions. The effect of experimental uncertainties on $A_c$, $\alpha$ and $v_F/v_2$ is indicated; the error on $\Delta_0$ is neglected.
| $B$(T) | orientation | $\gamma(B)$ [mJ/K$^2$mol] | $\Theta_D$ (K) | r.m.s. error [mJ/K$^2$mol] | number of data |
|--------|-------------|-----------------------------|-----------------|-----------------------------|----------------|
| 0      | [001]       | 2.19                        | 422.3           | 0.035                       | 357            |
| 0      | [100]+[010] | 2.17                        | 423.0           | 0.042                       | 647            |
| 0      | [110]       | 2.20                        | 423.4           | 0.025                       | 305            |
| 8      | [100]+[010] | 2.79                        | 427.4           | 0.047                       | 514            |
| 8      | [110]       | 2.75                        | 426.7           | 0.039                       | 301            |
| 14     | [100]+[010] | 2.96                        | 425.6           | 0.049                       | 210            |
| 14     | [110]       | 2.92                        | 425.6           | 0.057                       | 723            |

**TABLE II.** Results of fits of the high field specific heat for $B \perp c$: coefficient of the linear term $\gamma(B)$ and Debye temperature $\Theta_D$. The Schottky correction is fixed and corresponds here to 0.007% spin-1/2 per Cu atom with $g = 2.2$ and $B_{\text{int}} = 0.5$ T. The data in $B = 0$ with 3 orientations with respect to the magnet axis are shown only to document the reproducibility, since the bulk $C \propto T^2$ $d$-wave term is not included in the fit (attempts to include it yield values that are strongly correlated with $B_{\text{int}}$ and $\Theta_D$ and do not improve significantly the fit).
\[ C/T \ (\text{J/K}^2\text{g.at}) \]

\[ T \ (\text{K}) \]

- \( T_c = 87.80 \text{ K} \)
- 61 mJ/K\(^2\)mol
\frac{(C - \beta T^3)}{T} (\text{mJ/mol-K}^2)

(a) Ref. [8]

(b) this work

\begin{itemize}
  \item \(B[T]\)
  \item 0T
  \item 0.5T
  \item 2T
  \item 4T
  \item 6T
  \item 8T
\end{itemize}
\( \frac{C}{T} \text{ (mJ/K}^2\text{gat)} \) vs. \( T^2 \) (K\(^2\))
$\frac{[C(B)-C(8T)]}{T}$ (mJ/K$^2$g)at $T$ (K)

- $14 \, T$
- $4 \, T$
- $1 \, T$
- $B=0$
The graph shows the variation of \( \frac{[C(B) - C(0)]}{T} \) (in \( \text{mJ/K}^2 \cdot \text{g.at} \)) with magnetic field strength \( B(T) \) for different temperatures: T = 2K, T = 3K, and T = 4K.
\[ \frac{[C(B) - C(0)]}{TB^{1/2}} \text{ (mJ/K}^{3/2}\text{gat)} \]

\[ \frac{T}{B^{0.5}} \text{ (K/T}^{0.5}) \]
\[
\frac{[C(B) - C(0)]}{T} \text{ (mJ/K.g})
\]

\[B^{1/2} (T^{1/2})\]

Data:
- \(T = 2K\)
- \(T = 3K\)
- \(T = 4K\)

Models:
- \(T = 0\)
- \(T = 2K\)
- \(T = 3K\)
- \(T = 4K\)
$\frac{[C(B)-C(0)]}{T}$ (mJ/K²gat) vs $B$ (T)

- **1.4K**
- **2 K**
- **3 K**
- **4 K**
\[
\frac{[C(B) - C(0)]}{(TB^{1/2})}
\] (mJ/K^2T^{1/2}\text{gat})

![Graph showing temperature-dependent data](image-url)
\[ \frac{[C(B) - C(0)]}{TB^{1/2}} (\text{mJ/K}^{2}T^{1/2}_{gat}) \]

Graph showing data points for different temperatures and magnetic field directions.