Low-Temperature Specific Heat of $YBa_2Cu_3O_{7-\delta}$, $0 \leq \delta \leq 0.2$: Evidence for d-Wave Pairing

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The dependence of the specific heat of $YBa_2Cu_3O_{7-\delta}$ on temperature (T) and magnetic field (H) shows a number of features predicted for d-wave pairing: a T^2 term for $H = 0$ and an $H^{1/2}T$ term for $H \neq 0$ and low T, with a crossover to a stronger T dependence at higher T. For all H and T, these results are consistent with a recently proposed scaling relation. Values of the parameters derived from experimental data agree with theoretical predictions. [S0031-9007(99)08481-1]

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There is a growing consensus, based primarily on tunneling and vortex-imaging experiments that give information on the symmetry of the order parameter [1], that the superconductivity of $YBa_2Cu_3O_{7-\delta}$ (YBCO) involves d-wave pairing. Nevertheless, there is still considerable interest in the evidence of d-wave pairing that might be found in bulk properties, and the specific heat (C) is the obvious candidate. The electron density of states (DOS), its contribution (C_{DOS}) to C, and particularly the dependence of that contribution on magnetic field (H) are expected to be very different for d-wave and s-wave pairing. Measurements of $C(H)$ can therefore contribute to the evidence bearing on the nature of the pairing. They also give values of the DOS for comparison with model calculations of the quasiparticle excitation spectrum.

In the superconducting state it is expected on quite general grounds that a line of nodes in the energy gap associated with d-wave pairing gives $C_{\mathrm{DOS}}(0)$ a T^2 dependence [2,3] in place of the exponential dependence characteristic of the gap without nodes in s-wave superconductors. In the mixed state an $H^{1/2}T$ term has been predicted for a d-wave superconductor at low T [4,5], but with a crossover at a value $z_c \sim H_{c2}^{-1/2}T_c$ of the parameter $z \equiv H^{-1/2}T$ to a high-T, low-H region in which both a T^2 term that is independent of H, and a T-independent H-proportional term appear [3]. These terms arise from a Doppler shift of the quasiparticle excitation spectrum in the outer regions of the vortices, and the crossover reflects a change in the intervortex separation. These predictions are all consistent with a scaling relation derived on the basis of general considerations of the low-energy quasiparticle excitation spectrum of a d-wave superconductor, $C_{\mathrm{DOS}}/H^{1/2}T = F(H^{-1/2}T)$, where F is an undetermined scaling function [6].

The T^2 and $H^{1/2}T$ terms were first identified in experimental data by Moler *et al.* [7], in a Stanford/UBC collaboration. Their conclusions were based on a "global" fit, one in which data for all H were analyzed simultaneously with a T^2 term (αT^2) included in the fitting expression for $H = 0$. LBNL data gave similar results when fitted in the same way [8], but in both cases a fit to the zero-field data alone gave negative values of α, and it was concluded that the evidence for a T^2 term was not convincing [8]. Determining the contribution (C_{mag}) of paramagnetic centers (PC's) to C was a major source of ambiguity in the conclusions about the T^2 term. With respect to the $H^{1/2}T$ term, however, the Stanford/UBC and LBNL results are in good agreement [8]. On the other hand, recent data from the Geneva group [9], which give no evidence bearing on the reality of the T^2 term, show a significantly different dependence of the mixed-state C_{DOS} on both H and T.

We report here data on two new samples that have relatively low concentrations of PC's, for one of which C_{DOS} was determined for different carrier concentrations by making stepwise changes in the oxygen content and remeasuring C [10]. The use of a more accurate expression for C_{mag} that has no H-dependent adjustable parameters [10] and the low concentrations of PC's make possible a more reliable analysis of the $H = 0$ data. In the common interval of T, the results are in qualitative agreement with the Stanford/UBC report in showing a zero-field T^2 contribution as well as the $H^{1/2}T$ term. At higher T they show clear evidence of the predicted crossover. For all H and T they are consistent with the proposed scaling relation. In addition, the new results suggest that the d-wave effects are not very sensitive to impurities or, for $0 \leq \delta \leq 0.1$, to carrier concentration.

In addition to C_{DOS}, $C(H)$ includes four other contributions that together constitute a "background" specific heat (C_{bkgd}),

$$C(H) = C_{\mathrm{DOS}}(H) + C_{\mathrm{bkgd}}(H), \tag{1}$$

$$C_{\mathrm{bkgd}}(H) = C_{\mathrm{mag}}(H) + C_{\mathrm{hyp}}(H) + C_{\mathrm{lat}} + \gamma^*(0)T, \tag{2}$$

where $C_{\mathrm{mag}}(H)$ is the contribution of the PC's; $C_{\mathrm{hyp}}(H) = D(H)T^{-2}$ is primarily a hyperfine contribution; C_{lat} is the H-independent lattice contribution; $\gamma^*(0)T$ is the zero-field, T-proportional ("linear") term. (See Ref. [10] for further discussion.) Preliminary examination of the data showed the crossover at $z_c \sim 6.5T^{-1/2}$ K. Accordingly, the "basic" fit to the data, a global fit, was made with the theoretical expressions for C_{DOS} for $z < z_c$: αT^2 for

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$H = 0$, and $\Delta\gamma^*(H)T$ for $H \neq 0$. For $z > z_c$ the data points were omitted from the fit, and $C_{\rm DOS}$ was calculated using $C_{\rm bkgd}$ as determined in the fit. The T dependence predicted for $C_{\rm DOS}$ for $H \neq 0$ and $z < z_c$ was incorporated in the fitting expression, as $\Delta\gamma^*(H)T$, but its validity as a representation of the experimental data was tested in several ways [10]. However, the H dependence was left open: $\Delta\gamma^*(H)$ was determined independently for each H.

The results of the fit for sample DW54A are shown as $C_{\rm DOS}/T$ in Fig. 1(a), where the solid symbols represent the omitted data points. For $H = 0$, $C_{\rm DOS}$ shows the predicted T^2 dependence; the line through the points represents the value of α determined in the fit, 0.064 mJ K^{-3} mol^{-1}. For $H \neq 0$ and $z < z_c$, $C_{\rm DOS}/T = \Delta\gamma^*(H)$; the horizontal lines correspond to the values of $\Delta\gamma^*(H)$ determined in the fit. For $H \neq 0$ and $z > z_c$, the data points (solid symbols) deviate from the horizontal lines, and they are approximated by the sloping lines, which are parallel to the line through the $H = 0$ data. For $H = 0.5$ and 1 T, the changes in the slope at $T \sim 5$ and 6 K mark the crossover. (These changes in the slope are the basis for, not consequences of, the exclusion of the higher-T points from the fit: A fit to all the data gives essentially the same changes in the slope, as deviations from the fit, but slightly different values of some parameters.) Of the two terms in $C_{\rm DOS}$ predicted for $z > z_c$, it is the T^2 term that is suggested by the data. The other, an H-proportional T-independent term, would give a negative slope to the data for $T \gtrsim 5$ K and $H = 0.5$ T in Fig. 1(a). The crossover is also surprisingly sharp: A simple fit with a T-independent DOS that matches the limiting slopes of the 0.5-T data gives a width of ~5 K.

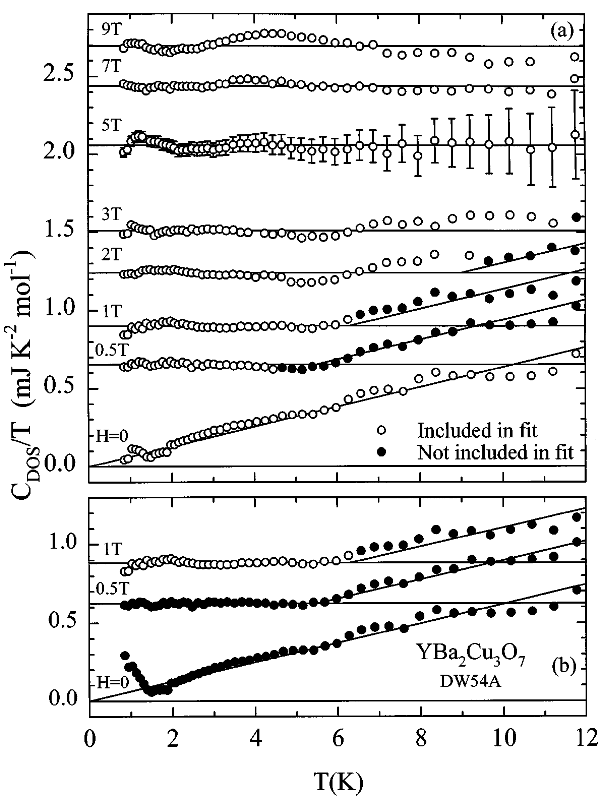

FIG. 1. $C_{\rm DOS}$ as obtained in two fits in which different points, shown as solid circles, were omitted: (a) the basic fit; (b) a fit with all 0- and 0.5-T data omitted. All lines that are not horizontal have the same slope, that of the fit to the $H = 0$ data in (a). The error bars on the 5-T points represent $\pm 0.5\%$ $C(H)/T$. They would be approximately the same for all H.

The new expression for $C_{\rm mag}(H)$ makes possible a more direct examination of the $H = 0$ data for a T^2 term. With the exception of $C_{\rm hyp}$, which is important only near and below 1 K, the contributions to $C_{\rm bkgd}$ can be determined for any H without using the data for that H, because there are no H-dependent adjustable parameters in the new expression for $C_{\rm mag}(H)$, and the other terms in $C_{\rm bkgd}$ are independent of H. Figure 1(b) shows the result of a fit in which the $H = 0$ data and all the $H = 0.5$ T data were omitted, and $C_{\rm DOS}$ calculated using $C_{\rm bkgd}(H)$ determined by the data for all other H. The sloping lines correspond to the value of α determined in the basic fit. Except for the low-T upturn in the $H = 0$ data, which is the $C_{\rm hyp}(0)/T$ that was not determined in that fit, the results are essentially identical to those obtained in the basic fit. For $H = 0$, they confirm the existence of the T^2 term and the validity of the value of α obtained in a global fit to all the data. (For $H = 0.5$ T, they provide additional evidence that the change in the slope is not a consequence of omitting some points from the fit and including others.)

For $z < z_c$, $C_{\rm DOS}$ is in excellent agreement with the predicted $H^{1/2}T$ dependence, $C_{\rm DOS} = \Delta\gamma^*(H)T = \beta H^{1/2}T$, with $\beta = 0.91$ mJ K^{-2} T$^{1/2}$ mol^{-1}, as shown by the solid triangles in Fig. 2. The open triangles in Fig. 2 demonstrate a relation between the zero-field T^2 term and the $H^{1/2}$ proportionality of $\Delta\gamma^*(H)$ that is inherent in the experimental data and supports the conclusion that both are real. They represent values of $\Delta\gamma^*(H)$ derived with the T^2 term omitted from the fitting expression. That

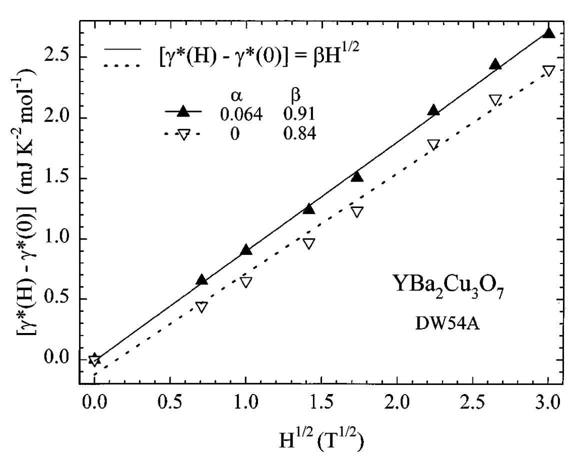

FIG. 2. $\Delta\gamma^*(H)$ as obtained in the basic fit (solid triangles) and in one with no T^2 term in the fitting expression (open triangles), with a least-squares fit to an $H^{1/2}$ dependence for each.

omission more than doubles the rms deviation from an $H^{1/2}$ least-squares fit to $\Delta\gamma^*(H)$, and the deviation from the fit of $\Delta\gamma^*(0)$, the point that is necessarily most affected, is particularly conspicuous. Within the uncertainty inherent in other quantities that enter into the comparison, the values of parameters derived from experimental data are in satisfactory agreement with theoretical predictions for α [2,3], β [4], and z_c [3], giving additional support to the d-wave interpretation.

Most results, both experimental [11] and theoretical [12], on the mixed-state C_{DOS} for conventional s-wave superconductors give an HT dependence in place of the $H^{1/2}T$ found for YBCO, but there are several exceptions that deserve comment. Measurements on V_3Si showed a negative curvature of $C(H)$ vs H and led to the suggestion that this behavior, sometimes approximating the $H^{1/2}$ dependence reported for YBCO, was a general feature of superconductors in the mixed state [13]. However, there are several reasons for questioning the relevance of that conclusion to the $H^{1/2}T$ term in YBCO: $C(H)$ was linear in H except near H_{c1}; the measurements were made on a zero-field-cooled sample in increasing H, and the curvature largely disappeared in decreasing H; other measurements on V_3Si in the same region of H, but made on a field-cooled sample in constant H, gave a positive curvature [14]. Also very relevant to any comparison with YBCO is the general expectation, and its experimental verification [15], that the low-energy excitations in the vortex cores that produce the HT term in conventional superconductors [12] are precluded in the cuprate superconductors by the small size of the cores. On the theoretical side it has also been suggested that the deviations from linearity in H for both YBCO and V_3Si might be understood as arising from the high density of low-energy states shown in a random-matrix model, but the calculation does not give an estimate of the magnitude or a prediction of the form of the deviation [16]. Although the mixed-state C_{DOS} of s-wave superconductors may not be fully understood, the preponderance of evidence suggests an approximate HT dependence, and it is reasonable to conclude that the $H^{1/2}T$ dependence in YBCO is a manifestation of d-wave pairing.

The results of the basic fit are in excellent agreement with the proposed scaling relation [6], as shown in Fig. 3 in a plot of $C_{\mathrm{DOS}}/H^{1/2}T$ vs z. For $z \leq z_c$ almost all the points fall within $\pm 5\%$ of a horizontal straight line, corresponding to the $H^{1/2}T$ dependence demonstrated in Figs. 1(a) and 2: The test of the scaling relation can be extended to $H = 0$ by rewriting it in the form $C_{\mathrm{DOS}}/T^2 = z^{-1}F(z)$ and plotting C_{DOS}/T^2 vs z^{-1}, as in Fig. 4. The deviations from the horizontal straight line at $z \sim 6.5\ \mathrm{T}^{-1/2}\,\mathrm{K}$ in Fig. 3 then appear as deviations from the straight line at $z^{-1} \sim 0.15\ \mathrm{T}^{1/2}\,\mathrm{K}^{-1}$. It is apparent that these deviations are consistent with a smooth extrapolation to the single point at $z^{-1} = 0$ that represents the $H = 0$ data by the value of α obtained in the basic fit. The error bars on that point represent the spread of $C_{\mathrm{DOS}}(0)/T^2$ calculated for the 32 individual data points

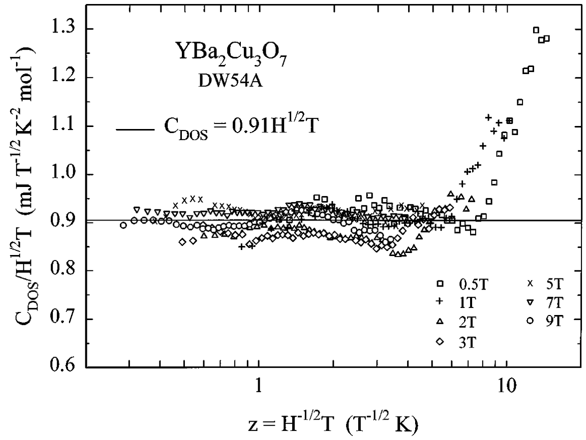

FIG. 3. A test of the scaling relation.

for which $\alpha T^2/C(0)$ is 2%–3.5%; error bars at 0.04 and 0.11 $\mathrm{mJ\,K^{-3}\,mol^{-1}}$ would encompass the other 18 points, for which that ratio is 1%–2%.

For sample DW41A, $C(H)$ was measured for different values of δ. For $\delta = 0$, 0.022, 0.044, 0.066, and 0.096, the values of α were 0.044, 0.059, 0.081, 0.062, and 0.062 $\mathrm{mJ\,K^{-3}\,mol^{-1}}$; the values of β were 0.82, 0.66, 0.72, 0.72, and 0.71 $\mathrm{mJ\,K^{-2}\,T^{-1/2}\,mol^{-1}}$, respectively. For higher values of δ, α was immeasurably small, and there were systematic deviations of $\Delta\gamma^*(H)$ from the proportionality to $H^{1/2}$. It is difficult to estimate the uncertainties in the values of these parameters but, particularly for α, they are substantial, and the variations with δ for $\delta \leq 0.1$ should be interpreted with caution.

The data for samples DW54A and DW41A are similar to those reported earlier for another polycrystalline sample, DP6 [8]. The most important features of the data for all three of these samples are, at least qualitatively, the same as those for the single crystal studied by Moler *et al.* [7] and also for that sample after detwinning [17]. For each of these five samples, measured in three different

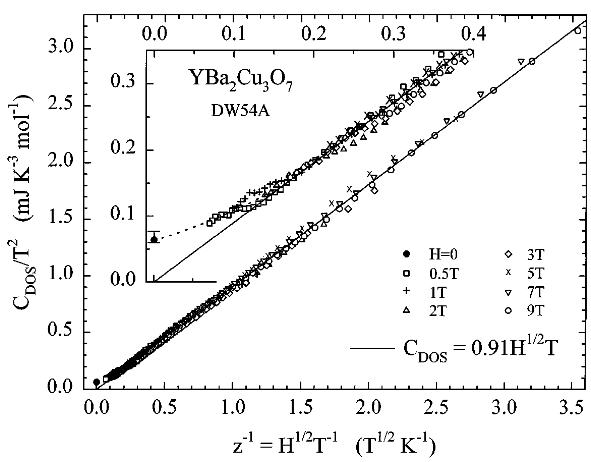

FIG. 4. A test of the scaling relation that includes $H = 0$ data. The inset is an expanded view of the same data for low z^{-1}.

calorimeters with three independently derived temperature scales, including DW41A for $0 \leq \delta \lesssim 0.1$, a global analysis gave a T^2 term in $C(0)$ and, for $H \neq 0$ and $T \leq 7$ K (the upper limit of the analysis of the Stanford/UBC data), $C_{DOS} \propto H^{1/2}T$. (The effects on the derived values of α and β of the difference between data for single crystals and polycrystals, differences in other parameters characteristic of the samples, and variations in fitting procedures have been considered elsewhere [8].) The Geneva group has reported no evidence bearing on the T^2 term but it has reported results of several measurements of C_{DOS} for $H \neq 0$ that differ substantially among themselves and with the LBNL and Stanford/UBC results. For one single crystal $C_{DOS}(H)$ was obtained by subtracting data for $H \parallel ab$ from data for $H \parallel c$ and assuming that all other contributions to $C(H)$ canceled [9]. $C_{DOS}(H)$ was not proportional to T; the H dependence of C_{DOS} was stronger at lower T; in a plot similar to that in Fig. 3, the data are best represented by a straight line with a pronounced negative slope that would appear at $\sim 45°$ to the horizontal. Data for another single crystal treated in the same way (Ref. [18], see Figs. III 3, 15, 16) and two polycrystalline samples (Ref. [18], see Figs. III 13, 14) all gave a C_{DOS} that was not proportional to T, but the dependence on H was different in each case and generally stronger at *lower* T for the polycrystalline samples.

For sample DW54A ($\delta = 0$), $\alpha = 0.064$ mJ K^{-3} mol^{-1}; for sample DW41A the five values of α for $0 \leq \delta \lesssim 0.1$ fall in the range of 0.044–0.081 mJ K^{-3} mol^{-1}, with no systematic trend with δ. For another YBCO sample for which the data support an analysis for the T^2 term, $\alpha = 0.055$ mJ K^{-3} mol^{-1} [8]. For a single crystal, before [7] and after [17] detwinning, values of 0.11 ± 0.02 and 0.10 ± 0.06 mJ K^{-3} mol^{-1}, respectively, have been reported, but there is some reason to think that smaller values might have been obtained had the data extended to a lower temperature [8]. Although the reality of the T^2 term is well established, the uncertainty in its magnitude is clearly substantial, and it seems reasonable to conclude that, within the experimental error, α is the same for all of these samples, and to take $\alpha = 0.065 \pm 0.02$ mJ K^{-3} mol^{-1} as the probable value. The apparent sample independence of α is surprising in light of the theoretical expectation that it should be very sensitive to impurities [2], but it may be understandable in terms of the nature of the impurities and their effects on the superconducting properties. Two strongly sample-dependent quantities that reflect the presence of impurities are the coefficient of the zero-field, T-proportional term, $\gamma^*(0)$, and n_2, the total concentration of paramagnetic centers. Correlations of other parameters with n_2 suggest that PC's suppress superconductivity, possibly producing local normal regions with a spatial extent of the order of the coherence length and show that, regardless of the mechanism, they increase $\gamma^*(0)$ [19]. For the YBCO samples cited above as showing essentially the same value of α, the values of n_2 vary by a factor of 5; the concentrations of spin-2 PC's alone by a factor of 3; the concentrations of spin-$\frac{1}{2}$ PC's alone by a factor of 5. A possible explanation of the small effect of the concentrations of PC's on α is that the spin-$\frac{1}{2}$ PC's, which are in the CuO chains, are only weakly coupled to the superconductivity in the CuO_2 planes, and the spin-2 PC's, which are in the planes, produce local normal regions without affecting the superconductivity elsewhere [10]. It has also been shown that twin boundaries contribute to $\gamma^*(0)$ [17]. Perhaps they, and other physical defects, also produce small-scale normal regions without otherwise affecting the superconducting properties.

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Note added.—Some of the features interpreted here as evidence for d-wave pairing in YBCO have also been seen in $(La_{1.85}Sr_{0.15})CuO_4$ [20].

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