Specific Heat of $YBa_2Cu_3O_7$: Origin of the "Linear" Term and Volume Fraction of Superconductivity

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Correlations of the coefficient of the "linear" term in the specific heat, $\gamma(0)$, and the discontinuity at T_c, $\Delta C(T_c)$, with a measured concentration of Cu^{2+} magnetic moments suggest the operation of a pair-breaking mechanism that limits the transition to the superconducting state and produces a contribution to $\gamma(0)$. There is no evidence for the existence of an intrinsic contribution to $\gamma(0)$. The value of $\Delta C(T_c)$ for a sample provides a measure of the volume fraction of superconductivity and a basis for correcting measured values of parameters to those characteristic of the fully superconducting state. Estimates of several quantities relevant to the strength of coupling are given.

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One of the interesting features of the high-T_c Cu-oxide superconductors is the occurrence of a "linear" term $\gamma(0)T$ in the specific heat C at low temperature and in zero magnetic field. This term is consistent with the resonating-valence-bond theory,[1] and suggests more generally the absence of the energy gap that is characteristic of conventional superconductors. For these reasons it has attracted considerable attention, but there is still no consensus as to its origin or significance. For $YBa_2Cu_3O_7$ (YBCO), the most intensively investigated of these materials, impurity phases such as $BaCuO_2$ can make significant contributions to $\gamma(0)$.[2] These phases contain Cu^{2+} magnetic moments that order near 10 K, producing very high values of C at temperatures of a few K—in just the window of temperature[3] in which $\gamma(0)$ is determined. However, the nature of the correlation of $\gamma(0)$ with estimates of the concentrations of the phases and the fact that values of $\gamma(0) \lesssim 4$ mJ/mol K^2 have not been observed have been taken as evidence that there is also an intrinsic contribution to $\gamma(0)$ that is characteristic of the superconducting state (see, e.g., Refs. 3 and 4).

In this Letter we summarize correlations between several sample-dependent parameters[5] for a number of YBCO samples. The combination of measurements on the same samples that is required to establish these correlations—C, both at low T and near T_c, and in magnetic fields; the magnetic susceptibility χ, from below T_c to high T—is unique to this work. In particular, it permits the independent determination of the concentrations of two types of magnetic moments: n_1, the concentration of the moments in impurity phases that order near 10 K; and n_2, the concentration of Cu^{2+} moments that order only below 1 K. The discontinuity in C at T_c, $\Delta C(T_c)$, and $\gamma(0)$, each of which is strongly sample dependent, are both correlated with n_2. The first of these correlations, a linear decrease in $\Delta C(T_c)$ with increasing n_2, shows that the n_2 moments are located in substantial measure on the YBCO lattice, a conclusion which is consistent with nuclear spin-lattice relaxation data[6] that show the presence of Cu^{2+} moments on the Cu plane sites. It suggests that the value of $\Delta C(T_c)$ in the $n_2=0$ limit is characteristic of an ideal, fully superconducting sample, and that a lower value of $\Delta C(T_c)$ measures a correspondingly lower volume fraction of superconductivity, f_s, thus providing a basis for correcting the measured values of other parameters to the values characteristic of the ideal superconducting state. The second correlation shows the existence of a significant, but hitherto unrecognized, n_2-proportional contribution to $\gamma(0)$ that, together with the n_1-proportional impurity-phase contribution, accounts for the measured $\gamma(0)$: There is no evidence for a nonzero $\gamma(0)$ in the limit that *both* n_1 and n_2 are zero. The two correlations of $\Delta C(T_c)$ and $\gamma(0)$ with n_2 are empirically independent but together they suggest that the n_2 moments act as pair-breaking centers, simultaneously limiting the transition to the superconducting state and producing a contribution to $\gamma(0)$. A preliminary report on this work has been presented elsewhere.[7]

For most YBCO samples, and for *all* that have been studied below 1 K, there is a zero-field "upturn" in C/T that is transformed[8] into a Schottky-like anomaly near 4 K in a field of 7 T. It is evidently associated with magnetic moments that order below 1 K in zero field. The Schottky anomaly is quantitatively consistent with Cu^{2+} moments, and determines their concentration n_2. The *total* concentration of Cu^{2+} moments, n, is derived from the high-T Curie-Weiss term in χ, and n_1 is obtained as $n_1=n-n_2$. These and other parameters characteristic of twelve samples, including two Zn-doped samples, are given in Table I. For one of the Zn-doped samples, the value of n_2 is within the range of values for the undoped

TABLE I. Derived parameters characteristic of the samples. Samples 8 and 9 were Zn doped, $YBa_2(Cu_{3-x}Zn_x)O_7$, with $x=0.03$ and 0.15, respectively. T_c is the temperature determined from the specific heat by an entropy-conserving construction. n and n_2 are moles Cu^{2+} per mole $YBa_2Cu_3O_7$. Other quantities are in mJ-mol-K-T units.

	n	n_2	$\gamma(0)$	$\Delta C(T_c)/T_c$	$d\gamma/dH$	T_c
1	0.015	0.0014	4.6	59	0.20	91
2	0.31	0.0023	6.4	71	0.24	90.5
3	0.049	0.0028	8.3	75	0.26	91
4	0.047	0.0031	7.4	60	0.22	90.5
5	0.027	0.0035	6.95	53	0.17	91.5
6	0.0044	0.0044	5.0	38	0.15	92.5
7	0.035	0.0048	8.6	43	0.145	92.5
8	0.022	0.0060	11	32	0.11	89
9	0.101	0.0089	23	0	0	⋯
10	⋯	0.0036	7.2	60	0.20	91
11	⋯	0.0060	11	36	0.14	92.5
12	⋯	0.0074	7.9	37	0.12	90

samples, and its properties are indistinguishable from those of the undoped samples. The sample with the higher Zn concentration extends the range of n_2 values by 20%, consistent with other evidence[9] that Zn doping increases the upturn in C/T and, therefore, n_2.

The values of $\Delta C(T_c)$ were determined by applying the usual entropy-conserving construction to data such as those shown in Fig. 1, and are shown in Fig. 2 as $\Delta C(T_c)/T_c$ vs n_2. [Since T_c is approximately constant for these samples, the n_2 dependence of $\Delta C(T_c)$ is the same as that of $\Delta C(T_c)/T_c$.] There is considerable scatter, which probably reflects not only the uncertainty in $\Delta C(T_c)$ but also the possibility that some of the magnetic moments counted in n_2 are in impurity phases and do not contribute to the effect on $\Delta C(T_c)$. However, the relation is roughly linear, and the value of $\Delta C(T_c)/T_c$, 77 mJ/mol K^2, characteristic of an ideal sample with $n_2=0$, was determined by fitting the data with the straight line shown in Fig. 2. For that purpose the point for sample 9, which showed a small Meissner effect but no measurable $\Delta C(T_c)$, was given zero weight because it seemed probable that $\Delta C(T_c)$ was not measurable only because the transition was too broad. The interpretation of the sample dependence of $\Delta C(T_c)$ as an indication of incomplete transitions to the superconducting state, with f_s given by the ratio of $\Delta C(T_c)$ to the ideal value, is consistent with other measures[5] of f_s, one of which, $d\gamma/dH$, is compared with $\Delta C(T_c)/T_c$ in Fig. 3. Since $\gamma(H)$ is approximately proportional to H for a superconductor in the mixed state, $d\gamma/dH$ should also be proportional to f_s. The proportionality of $d\gamma/dH$ to $\Delta C(T_c)$ displayed in Fig. 3 supports the interpretation of $\Delta C(T_c)$ as a measure of f_s, and the quality of the fit suggests that the larger scatter in the $\Delta C(T_c)/T_c$ vs n_2 plot arises in part from the inclusion in n_2 of Cu^{2+} moments that do not affect $\Delta C(T_c)$. Independently of the interpretation of the n_2 dependence of $\Delta C(T_c)$, the value of $\Delta C(T_c)$ provides a useful criterion for identifying the values of other parameters, e.g., $d\gamma/dH$, that are characteristic of the ideal superconducting state.

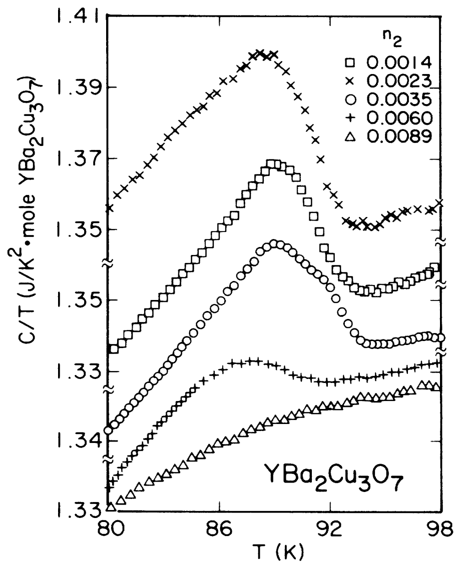

FIG. 1. C/T in the vicinity of T_c for samples 1, 2, 5, 8, and 9.

The solid triangles in Fig. 4 represent $\gamma(0)$ as a function of n, which, in the absence of independent measurements of n_2, has often been taken as a measure of the concentration of impurity phases. The correlation is similar to that reported by the Geneva group[10]—the data scatter widely, but the relation is approximately linear. A fit with $\gamma(0)=\gamma_0+\gamma' n$ gives $\gamma_0=2.5$ mJ/mol K^2 with an rms deviation of 34%. Taking n_1 and n_2 as independent variables, $\gamma(0)=\gamma_0+\gamma_1 n_1+\gamma_2 n_2$, gives $\gamma_0=0.1\pm0.8$ mJ/mol K^2, with an rms deviation of 11%, and eliminating the γ_0 term does not appreciably affect the fit. (The values of both γ' and γ_1 are reasonable in

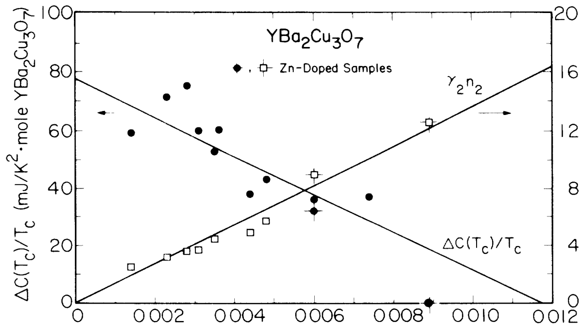

FIG. 2. $\Delta C(T_c)/T_c$ vs n_2. For comparison, $\gamma_2 n_2$ is reproduced from Fig. 4 on an expanded scale.

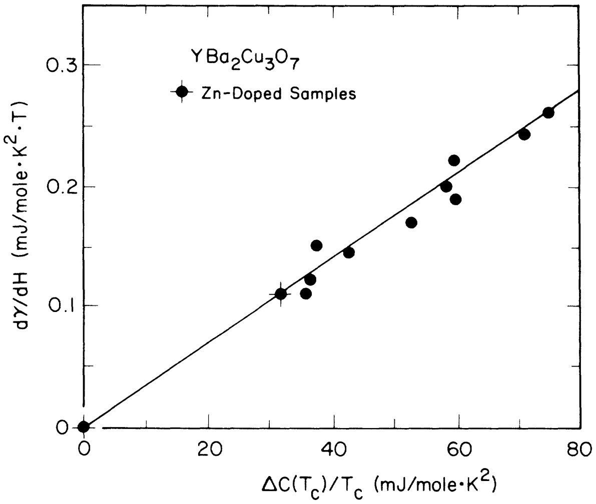

FIG. 3. Magnetic-field derivative of the coefficient of the linear term in C vs $\Delta C(T_c)/T_c$.

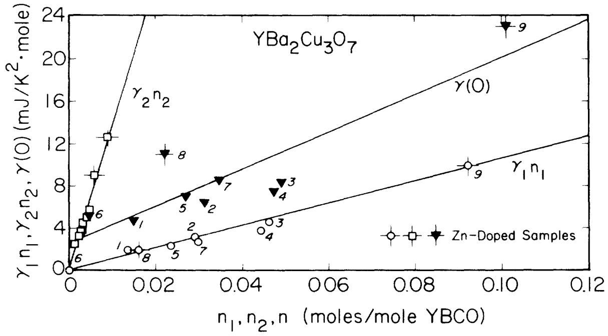

FIG. 4. $\gamma(0)$ and its components, $\gamma_1 n_2$ and $\gamma_2 n_2$, plotted against, respectively, n, n_1, and n_2, the concentrations of Cu^{2+} moments. Points are labeled with sample numbers (see Table I) which are in order of increasing $\gamma_2 n_2$. See text for other details.

relation to the properties[2] of $BaCuO_2$.) The n_1- and n_2-proportional components of that fit are represented by the open circles and open squares in Fig. 4. Uncertainty in the value of γ_0 arises both from the possibility that Zn doping affects the relevant parameters by other mechanisms as well as by the creation of Cu^{2+} moments, and from uncertainty in the correct "background" χ to use in calculating n. The values of n in Table I and Fig. 4 were calculated on the assumption of a temperature-independent background; they, and the values of n_1, would be increased by 0.03 if the temperature-dependent fluctuation term reported by Lee *et al.*[11] were included. Values of γ_0 ranging from -2 to 2 mJ/mol K^2 can be obtained depending on the choices made with respect to inclusion in the analysis of data for the Zn-doped samples and the fluctuation term in χ. However, in every case the fit is improved, by a factor of 3 in rms deviation, by the inclusion of a term in n_2. These results show the importance of an n_2-proportional contribution to $\gamma(0)$; and that for these samples, and within the experimental uncertainty, there is no evidence for a contribution that is an intrinsic property of the superconducting state. The Geneva group[12] has reached a similar conclusion by applying a different, but apparently related, criterion to the samples studied there. In some cases, the absence of an upturn in C/T has been taken as showing the absence of extraneous contributions and the intrinsic nature of the observed $\gamma(0)$. However, impurity phases can contribute to $\gamma(0)$ without showing an upturn,[2] and the observation of an upturn depends on the low-temperature limit of the measurements. There does not appear to be any sample[13] that is an obvious exception to the above correlation of $\gamma(0)$ with n_1 and n_2, or to the conclusion that the experimental data for YBCO do not demonstrate the existence of an intrinsic contribution to $\gamma(0)$.

Taken together with the $\gamma_2 n_2$ contribution to $\gamma(0)$, which is included in Fig. 2 for comparison, the approximately linear decrease in $\Delta C(T_c)$ with increasing n_2 suggests that the Cu^{2+} moments act as pair-breaking centers, an effect that is well established for magnetic moments in conventional superconductors. [It is, of course, possible that another mechanism produces both the observed effects on $\Delta C(T_c)$ and $\gamma(0)$, and Cu^{2+} moments. For example, nonmagnetic defects could be effective as pair-breaking centers if the electron pairing is not spin singlet.] There is, however, one conspicuous difference between YBCO and the gapless superconductivity associated with pair breaking in conventional superconductors: Gapless superconductivity in conventional superconductors is characterized by linear relations between $\Delta C(T_c)$, n_2, and $\gamma(0)$, but also by a linear decrease in T_c with increasing n_2—to $T_c = 0$ for a value of n_2 comparable to that for which $\Delta C(T_c) = 0$. The behavior of YBCO differs conspicuously from that of conventional superconductors in the n_2 dependence of T_c: For a value of n_2 for which $\Delta C(T_c)$ has decreased by more than a factor of 2, there is no significant change in T_c. The comparisons with pair breaking and gapless superconductivity in conventional superconductors suggest a somewhat different model, one that is also suggested by the very short coherence length ξ: Superconductivity is suppressed by the pair-breaking interaction, but because ξ is small the result is a mixture of normal regions in the vicinity of magnetic moments, and superconducting regions with T_c unchanged elsewhere, rather than gapless superconductivity with T_c uniformly depressed throughout the sample. The value of $\Delta C(T_c)$ is a measure of the volume fraction of superconductivity rather than an indication of the effect of n_2 on an order parameter that is characteristic of the sample as a whole. The model also has implications of interest for technical applications. It is widely believed that the low critical currents in bulk ceramic $YBa_2Cu_3O_7$ samples are associated with normal or weakly superconducting inclusions that separate the more perfectly superconducting regions—the "weak-link" effect. The value of $\Delta C(T_c)$

provides a measure of the volume fraction of these inclusions, and shows that even for samples prepared by methods believed to give good superconducting material there are substantial normal-state inclusions.

Other measurements on YBCO have given results that appear to be related to those reported here. They include the following: Tunneling measurements[14] on single crystals show a zero-bias conductance which is consistent with an approximately equal mixture of normal and superconducting regions. Specific-heat measurements[15] on single crystals typically give values of $\Delta C(T_c)$ of the order of 50% of the maximum value, even though the transitions are very sharp. Specific-heat measurements on samples irradiated with fast neutrons[16] show that with increasing neutron fluence $\Delta C(T_c)$ decreases; and the Curie-Weiss term in χ, the low-temperature upturn in C/T, and $\gamma(0)$ all increase —precisely the combination of effects associated with increasing n_2—showing that the Cu^{2+} moments are associated with physical defects as well as with chemical substitution on the Cu sites.

The interpretation of specific-heat data proposed here leads to estimates of the values of several parameters of interest in connection with the nature of both the superconducting and normal states. The coefficient of the normal-state electronic specific heat, γ, can be estimated in several ways: (1) By extrapolating the value of $d\gamma/dH$ for a fully superconducting sample, i.e., for $f_s=1$, $\Delta C(T_c)/T_c = 77$ mJ/mol K^2, to an appropriately averaged[5] value of the upper critical field,[17] one obtains $\gamma = 16$ mJ/mol K^2. (2) By extrapolating the $\gamma_2 n_2$ contribution to the value of n_2 at which superconductivity disappears, i.e., at which $\Delta C(T_c)=0$, one obtains $\gamma=16$ mJ/mol K^2. (3) By fitting the specific-heat data in the vicinity of T_c with the "α" model,[18] a semiphenomenological extension of the BCS theory that takes into account strong-coupling effects, one obtains a value for the energy-gap parameter $\alpha \equiv 2\Delta_0/k_B T_c$ which is independent of f_s, and, after using the value of $\Delta C(T_c)/T_c$ to correct to $f_s=1$, $\gamma = 14$ mJ/mol K^2. These and other estimates[5] of γ suggest $\gamma \sim 16$ mJ/mol K^2 as a "best," but very approximate, average. Extreme strong-coupling effects are suggested both by the ratio $\Delta C(T_c)/\gamma T_c = 4.8$ for a fully superconducting sample (cf. 1.43 for weak coupling) and by $\alpha = 7$ obtained by fitting with the α model (cf. $\alpha = 3.53$ for weak coupling). On the other hand, band-structure calculations[19,20] have given $\gamma_{\mathrm{bs}} = 13$ and 16 mJ/mol K^2 for the bare, or band-structure, contribution to γ. They lead to estimates of 0.2 and 0 for the electron-phonon interaction parameter $\lambda = (\gamma - \gamma_{\mathrm{bs}})/\gamma_{\mathrm{bs}}$, values much too small to be consistent with strong coupling. The resolution of this discrepancy, which has also been suggested by other lines of reasoning, is that the coupling between the electrons is strong but not (entirely) through the phonons.

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[13] The sample described in Ref. 4 and M. E. Reeves *et al.*, Phys. Rev. B **40**, 4573 (1989), deserves special notice because it was unusually well characterized. C was measured from 2 to 10 K, in fields to 3 T. The reported $\gamma(0)$, 4.37 mJ/mol K^2, was assumed to be intrinsic because no upturn in C/T was observed and an upper limit of 0.3 wt% was placed on the amount of BaCuO$_2$ ($n_1 = 0.009$). However, various possible nonintrinsic contributions could account for a significant fraction of $\gamma(0)$: The upper limit to the BaCuO$_2$ contribution is 1.4 mJ/mol K^2; the reported 2 wt% of Y$_2$BaCuO$_5$ would contribute 0.3 mJ/mol K^2; the reported anomalous field dependence of the T^3 term in C is equally well represented by the high-T side of a Schottky anomaly that corresponds to $n_2 = 9.5\times10^{-4}$ and a contribution to $\gamma(0)$ of 1.3 mJ/mol K^2 (the upturn in C/T at 2 K would be comparable to the precision of the data); and finally, *the high-T χ data show that 8%-12% of the Cu is present as Cu^{2+}* ($n = 0.24$-0.36), i.e., as other phases of unknown properties.

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