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SPECIFIC HEAT OF THE HIGH-T_c SUPERCONDUCTORS (La, M)$_2$CuO$_4$ AND YBa$_2$Cu$_3$O$_7$ IN MAGNETIC FIELDS[*]

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The specific heats, C, of the high-T_c superconductors YBa$_2$Cu$_3$O$_7$, La$_{1.85}$Ca$_{0.15}$CuO$_4$ and La$_{1.85}$Sr$_{0.15}$CuO$_4$ have been measured from 0.4 K to above the superconducting transition temperature in magnetic fields, H, from 0 to 7 T. From measured changes in C with H, values of $\gamma(H) = [C(H)/T]_{T=0}$ and $\Delta C/T_c = [(C_s - C_n)/T]_{T=T_c}$ have been evaluated. These results have been used to estimate the normal state γ, the fraction of the sample that is superconducting in zero field, f_s, and the value of the upper critical field, $[H_{c2}]_{T=0}$.

The specific heat, C, of a 22.7 g YBa$_2$Cu$_3$O$_7$ (YBCO) sample was measured using a standard heat pulse method from 0.4 to 30 K in zero magnetic field, H, and in fields of 3.5 and 7 T. The specific heat was also measured between 80 and 95 K by a continuous heating method ($\mathrm{d}T/\mathrm{d}t$ was about 1.5 mK/s) in zero field and at 7 T. An estimate of the precision for both types of measurements was about 0.1%. In zero field C/T below about 1.5 K has an upturn which may be intrinsic but is probably due to the presence of a magnetic impurity such as BaCuO$_2$. BaCuO$_2$ is usually present in YBCO, and furthermore, a spectroscopic analysis detected no other impurities at a level of <0.1 wt%. In fields of 3.5 and 7 T the C/T data clearly show Schottky-like anomalies, with maxima near 1.5 and 3 K, respectively, which are presumably due to the same magnetic impurity causing the upturn in zero field. From the amplitude of the maxima, and assuming two electronic states, the amount of impurity is estimated to be about 0.4 mol%. (Previous measurements on another YBCO sample had an anomaly in C/T near 1 K, which in all likelihood arose from a 1 mol% Cr impurity which was found in a subsequent spectroscopic determination.) Meissner effect measurements in $H = 8.62$ G (calibrated using the normal/superconducting transition in a Sn sphere) indicated an onset T_c of 92 K with a transition width (10–90%), ΔT_c, of 8 K. The sample had a flux exclusion $-4\pi\chi_V = 0.23$, based on the total volume of the sample and corrected for demagnetizing effects, assuming the cylindrical sample (diameter equal to height) could be approximated by a sphere of the same diameter.

The low temperature specific heat data were fitted to

$$C(H) = A(H)/T^2 + \gamma(H)T + B_3T^3 + B_5T^5 , \tag{1}$$

in the range T_L–15 K. T_L was selected so that the T^{-2} approximation to the Schottky anomaly was valid. (In 7 T, below about 1 K, there is also a T^{-2} component due to hyperfine contributions). All coefficients in eq. 1 were evaluated for one mole of YBCO, for which the molecular weight was taken as 666 g/mol. In zero field $\gamma(0)$ is 7.1 mJ/K^{2}mol YBCO. For 3.5 and 7 T, $\gamma(H)$ was, respectively, 7.8 and 8.6 mJ/K^2 mole YBCO. B_3 and B_5 were field independent to within about 1%, in contrast to the field depend-

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ence [1] of B_3 found for the (La, M)$_2$CuO$_4$ compounds. From B_3, a Debye temperature, Θ_D, of 430 K was evaluated from $B_3/13 = (12/5)\pi^4/\Theta_D^3$. Fig. 1 is a plot of $[C - C_1]/T$ vs. T below 20 K, which shows the anomalies due to the presumed magnetic impurity and the derived values of $\gamma(H)$ as horizontal lines. (The addenda heat capacity is not yet known to high accuracy. Final values of C for the sample will be reported in the future. The shape of the curves in fig. 1 may be slightly altered when the corrected addenda are subtracted).

While some current theoretical models for high T_c superconductors [2] predict a linear contribution to the specific heat in the superconducting phase, our tentative analysis of the experimental results assumes that the non-zero value of $\gamma(0)$ is evidence that in zero field a fraction of the sample remains in the normal phase down to the lowest temperatures measured. We emphasize that the experimental data do not permit a choice between these two possibilities.

The low temperature specific heat measurements on YBCO in magnetic fields of 3.5 and 7 T show that the γ increases approximately linearly with magnetic field, $d\gamma(H)/dH = 0.21$ mJ/K^{2}T mol YBCO. A similar dependence of γ on H has been observed in the (La, M)$_2$CuO$_4$ compounds (see table I) as well as in other type II superconductors.

For zero field, the heat capacity data show the anomaly associated with the normal/superconducting transition between 88 and 92 K. The anomaly is suppressed and shifted downward by the application of 7 T. The shift is consistent with the estimates of $[dH_{c2}/dT]_{H=0}$ of 1–5 T/K from magnetic measurements [3]. A plot of [C(sample) + C(addenda)]/T vs. T is shown in fig. 2.

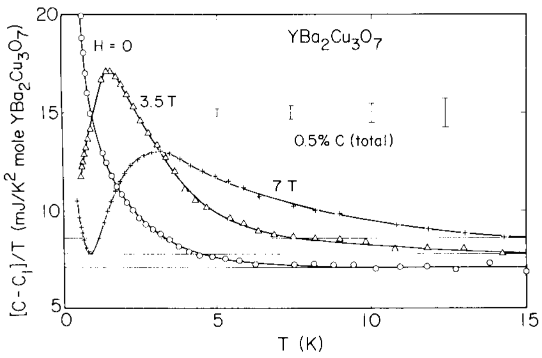

Fig. 1. $[C - C_1]/T$ vs. T for YBa$_2$Cu$_3$O$_7$. The heavy lines are spline fits to the data, while the light lines represent $\gamma(H)$ at 0, 3.5 and 7 T derived from fits to the data described in the text. In 7 T, below about 1 K, the upturn in C/T is due to hyperfine components of ^{63,65}Cu and ^{89}Y.

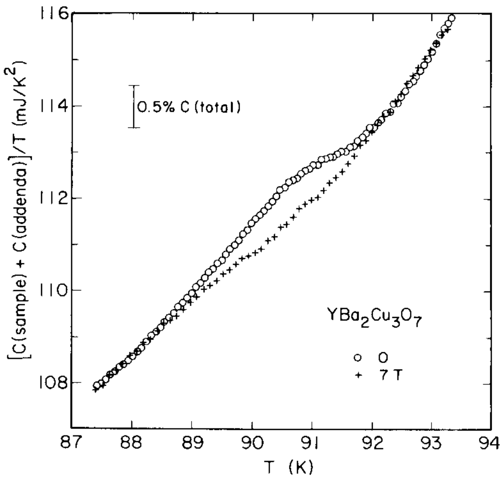

Fig. 2. [C(sample) + C(addenda)]/T vs. T for YBa$_2$Cu$_3$O$_7$ at $H = 0$ and 7 T. For clarity, only one-half of the data at each field are plotted. C was measured by a continuous heating method.

Table I
Parameters characterizing the high-T_c superconductors (La, M)$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_7$. (All units are in mJ, K and T).[a,b]

	$-4\pi\chi_V$	T_c	ΔT_c	$\gamma(0)$	$d\gamma/dH$	$B_3(0)$	dB_3/dH	B_5	Θ_D	f_s	$\Delta C/T_c$	γ
Cal	0.26	22	6	3.05	0.035	0.145	0.0019	0.0013	450	0.31	1.92	4.4
Sr2	0.35	37	8	1.54	0.109	0.168	0.0011	0.00085	430	0.82	9.9	8.6
Y2	0.23	92	8	7.1	0.21	0.32	0	0.0008	430	0.79	38	34

[a] $\Delta C/T_c$ are the ideal transition discontinuities from entropy conserving constructions of the broadened measured $\Delta C/T_c$.
[b] γ is derived assuming $\Delta C/T_c$ (ideal) $= 1.43 f_s \gamma$.

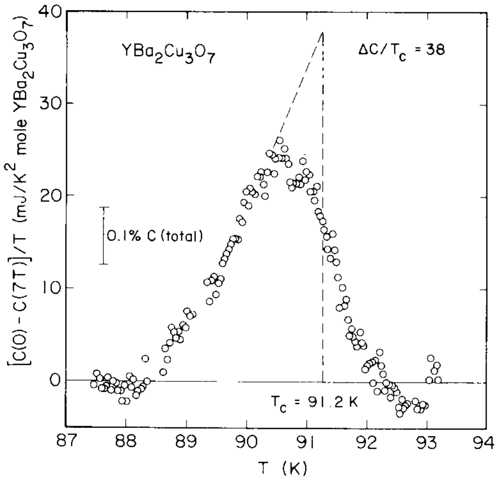

Fig. 3. $[C(0) - C(7\,T)]/T$ vs. T for $YBa_2Cu_3O_7$ showing the onset of the normal/superconducting transition near 92 K. The dashed vertical line is the idealized, entropy-conserving construction for a sharp transition at T_c.

Since the heat capacity of the addenda has not been measured in the 80–100 K region, absolute specific heat results cannot yet be obtained from these data. However, subtraction of the 7 T data from the zero field data (shown in fig. 3) does permit an evaluation of an ideal $\Delta C/T_c \approx 38\ \mathrm{mJ/K^2 mol}$ YBCO, comparable to the value of $39\ \mathrm{mJ/K^2 mol}$ YBCO obtained by Junod et al. [4]. If we assume that BCS theory is applicable, and that only a fraction, f_s, of the sample is superconducting, then $\Delta C/T_c = 1.43 f_s \gamma$, where γ is the coefficient of the linear contribution to the specific heat of the normal material. Since $\gamma(0) = (1 - f_s)\gamma$, we can use these two relations, plus the experimental results $\Delta C/T_c = 38\ \mathrm{mJ/K^2 mol}$ YBCO and $\gamma(0) = 7.1\ \mathrm{mJ/K^2 mol}$ YBCO, to obtain $\gamma = 34\ \mathrm{mJ/K^2 mol}$ YBCO and $f_s = 0.79$. From our results, and the assumption that $\gamma(0) = \gamma - [\mathrm{d}\gamma(H)/\mathrm{d}H][H_{c2}]_{T=0}$, we estimate that for YBCO $[H_{c2}]_{T=0} = 130\,\mathrm{T}$, a value which is in the range of other estimates [3]. (It is, or course, possible that the linear dependence of γ on H breaks down for sufficiently large applied magnetic fields. Our value for $[H_{c2}]_{T=0}$ should probably be regarded as a lower bound on the actual value).

Table I contains a summary of the results on YBCO. For purposes of comparison, we have included our data on $La_{1.85}M_{0.15}CuO_4$, where M = Ca and Sr. These latter results have been described in detail elsewhere [1].

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