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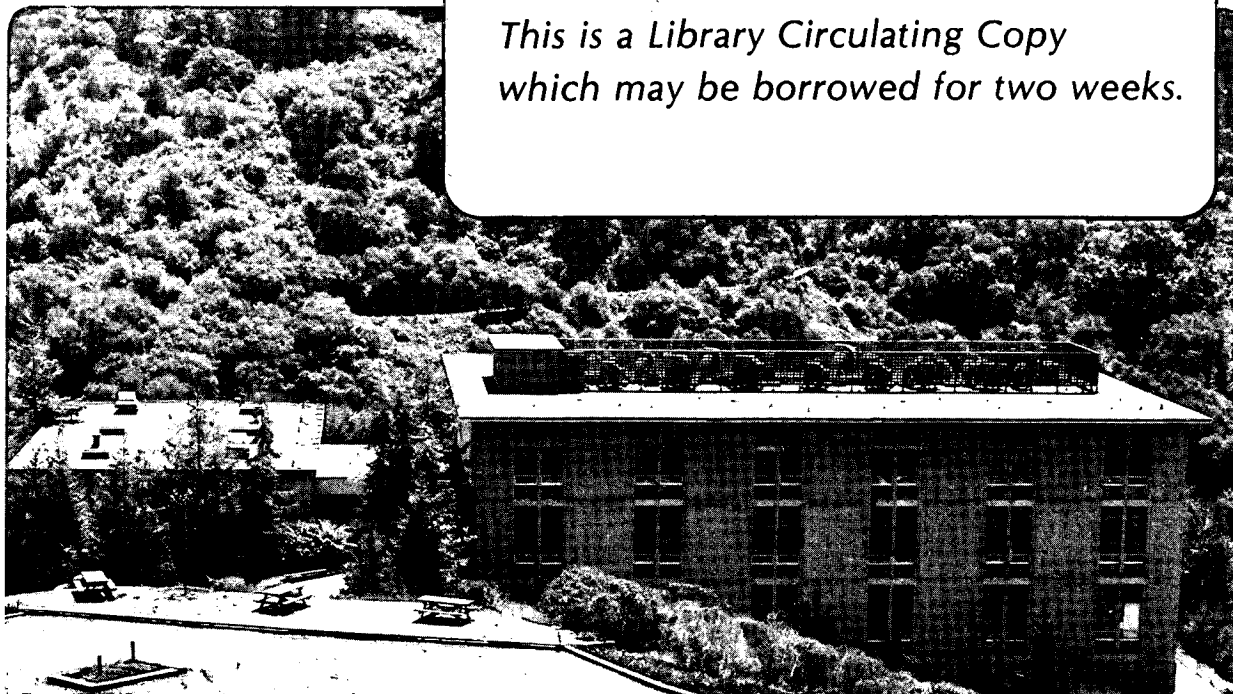
### Specific Heat of $\text{YBa}_2\text{Cu}_3\text{O}_7$

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## SPECIFIC HEAT OF $\text{YBa}_2\text{Cu}_3\text{O}_7^*$

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The specific heats of five  $\text{YBa}_2\text{Cu}_3\text{O}_7$  samples were measured in the range 0.4-100K in fields of 0, 3.5 and 7T. For two samples Cr was partially substituted for Cu. This produced only a small decrease in  $T_c$  (0.35 K/mole % Cr) but a strong suppression of the Meissner effect and  $\Delta C/T_c^c$ , which provided a basis for estimating the normal-state specific heat near  $T_c^c$ . A third sample had Cr present in an impurity phase. Two undoped samples showed evidence of fluctuation effects near  $T_c$ . A comparison of these results with other work is given.

Of the 5 samples of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBCO) studied, one, Y1, was accidentally contaminated with Cr, and had a composition corresponding to  $\text{YBa}_2\text{Cu}_{3-x}\text{Cr}_x\text{O}_7$  with  $x \approx 0.08$ . The specific heat (C) of this sample, which was measured only below 30K, showed clear evidence of localized magnetic moments that ordered in zero magnetic field near 1.5K (1). On the assumption that the Cr had substituted on the Cu sites, it was decided to investigate the effect of varying x on the Cr ordering and other features of the specific heat, and Y4 and Y5 were made with  $x = 0.015$  and 0.040, respectively.

All samples were characterized by Meissner effect measurements and the values obtained for the onset  $T_c$  and  $\Delta T_c$  (10 to 90%) are reported, along with other experimentally determined parameters, in Table I.  $\gamma(0)$  is the coefficient of the zero-field linear term in C,  $\partial\gamma/\partial H$  is the field dependence of the linear term measured directly at low temperatures,  $\gamma$  is the value deduced from  $\Delta C(T_c^c)$ ,  $\theta_D$  is the Debye temperature, and  $B_3$  and  $B_5$  are the coefficients of the  $T^3$  and  $T^5$  terms in the lattice specific heat.

Specific heat data for Y3 are shown in Fig. 1. The data near  $T_c$  are more precise than for other samples, and are shown for that reason, but this sample is also unusual in showing structure in C that is suggestive of a (broadened) step-wise transition. The upturn in C/T at low temperature is typical of that observed for the other samples (and also for YBCO samples studied elsewhere) except that in Y1 the upturn is larger, occurs at a higher temperature, and peaks near 1.5K. This difference between Y1 and samples Y4 and Y5, the fact that  $T_c$  for Y1 was not depressed by the Cr, and also the fact that Y1 exhibits a Schottky anomaly in 7T consistent with the value of x and the occurrence of localized moments on the Cr ions, suggest that in Y1 the Cr was in an impurity phase, and that the ordering of the Cr was not associated with Cr substituted on the Cu sites.

The analysis of C into its components -- lattice,  $C_l$ ; electronic,  $C_e$ ; impurity,  $C_i$ ; and hyperfine,  $C_h$  -- is shown for Y3 in three magnetic fields in Fig. 2. The low temperature upturn in C,  $C_i(0)$ , can be fitted by the high-temperature tail of a Schottky anomaly. In 3.5 and 7T,  $C_i$  could also be fitted by a Schottky anomaly by adjusting the spin (S) and g values (but not the entropy). This adjustment presumably made a crude allowance for the effects of internal fields, which are clearly not negligible. The impurity concentration,  $n_i$ , (see Table I) was derived from the  $S=1/2$ ,  $g=2.3$  Schottky anomaly fitted to

the data in 7T. The linear, electronic term in C,  $C(H) = \gamma(H)T$ , is adequately defined by the data between 1 and 5K, and was found to be linear in H, as observed for conventional type II superconductors.

The field dependence of C near  $T_c$  is shown in Fig. 3 for sample 3. The behavior differs from that of conventional type II superconductors in that the anomaly is diminished with increasing field but neither the temperature of the maximum in C/T nor the temperature of the onset of superconductivity is substantially affected. These features, which may reflect the importance of fluctuation effects, are similar to those observed in a single crystal (2) that showed a much sharper transition. The solid curve in Fig. 3 represents data for Y5, which shows no observable anomaly or field dependence in this temperature region, and which are therefore assumed to represent the normal state. Both the data for Y3 by themselves and the comparison with the curve for Y5 suggest that earlier estimates (3) of  $\Delta C(T_c)$  for Y2 from the difference between the zero field and 7T data are low. Here  $\Delta C(T_c)$  was estimated from the entropy conserving construction for Y3 shown in Fig. 4, and the values of  $\gamma$  deduced for the weak-coupling limit,  $\Delta C(T_c) = 1.43\gamma T_c$ , are given in Table I, along with corrected values for Y2.

Parameters derived from other specific heat measurements on YBCO are listed in Table II. The quantity  $\gamma(0)$  is of particular interest and it is interesting to note that many of the reported values fall in the range 6-9 mJ/mole  $K^2$ . Furthermore, the lower values may well arise from an extrapolation of C/T vs  $T^2$  from a temperature that is too high -- the effects of phonon dispersion are significant at 5K and in combination with the  $T^2$  term in C they tend to produce such an error in a simple analysis. This suggests that a  $\gamma$  value of the order of 6-9 mJ/mole  $K^2$  is an intrinsic property of YBCO, and not just a measure of the amount of nonsuperconducting material. Since  $\gamma(0)$  is not very dependent on oxygen content (4,5), it seems unlikely that it arises from two-level systems associated with oxygen vacancies, leaving an intrinsic electronic contribution such as that predicted in the RVB (6) model as the most probable origin.

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TABLE I. Parameters characterizing  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . [All units are in mJ, mole, K and T.  $n_i$  is moles/mole YBCO.]<sup>a</sup>

	$n_i$	$-4\pi\chi_V$	$T_c$	$\Delta T_c$	$\gamma(0)$	$\partial\gamma/\partial H$	$\Delta C/T_c^b$	$\gamma^c$	$H_{c2} _{T=0}^d$	$\theta_D^e$	$B_3$	$B_5$
Y1 <sub>f</sub>	0.08	0.28	91	9	-20	-0.3						
Y4 <sub>f</sub>	0.007	0.11	91.5	6	8.75	0.16	18		433	0.311	0.0012	
Y5 <sub>f,g</sub>	0.014	0.11	91	10	9.3	0.17	-0		432	0.313	0.0014	
Y2	0.005	0.23	92	8	6.8	0.20	52	36(43)	150(180)	452	0.273	0.0010
Y3	0.004	0.20	92	5	6.95	0.16	47	33(40)	160(210)	457	0.264	0.0011

(a) All of the samples had hyperfine components  $A_h(7)/T^2$  with  $A_h(7)$  ranging from 0.2-0.3 compared to 0.47 expected for Cu.

(b)  $\Delta C/T_c$  is the idealized entropy conserving discontinuity for a sharp transition using the solid curve shown in Fig. 4 for Y5 for which  $\Delta C/T_c$  was completely suppressed.

(c) Values of  $\gamma$  in parentheses were calculated from  $\Delta C/T_c = 1.43f_s\gamma$  assuming that  $\gamma(0)$  is a measure of the fraction of normal YBCO,  $f_n = (1-f_s)$ .

(d)  $H_{c2}|_{T=0} = [\gamma - \gamma(0)] / (\partial\gamma/\partial H)$ .

(e)  $\theta_D = 3\sqrt{(1.944 \times 10^6 N_D / B_3)}$  where  $N_D = 13$ .

(f) Samples Y4 and Y5 had the composition  $\text{YBa}_2(\text{Cu}_{2.985}\text{Cr}_{0.015})\text{O}_7$  and  $\text{YBa}_2(\text{Cu}_{2.960}\text{Cr}_{0.040})\text{O}_7$ , respectively, as determined from atomic absorption spectroscopy.

(g) Y5 was prepared by a different method which gave  $T_c = 92.5$ ,  $\Delta T_c = 5$  and  $-4\pi\chi_V = 0.40$  for an undoped sample.

TABLE II. Comparison of parameters derived from specific heat measurements on  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . [Units are K, T and mJ (for a gram formula weight--666g/mole YBCO).  $\Delta C/T_c$  is the ideal sharp entropy conserving discontinuity at  $T_c$ , equal to  $1.43\gamma$  in the weak coupling limit. At  $T=0\text{K}$   $\theta_D = 3/(1.944 \times 10^6 N_D/B_3)^{1/3}$  where  $N_D=13$ . Blanks indicate that the property was not determined while a  $\dagger$  for  $C_i(0)$  indicates detection.]

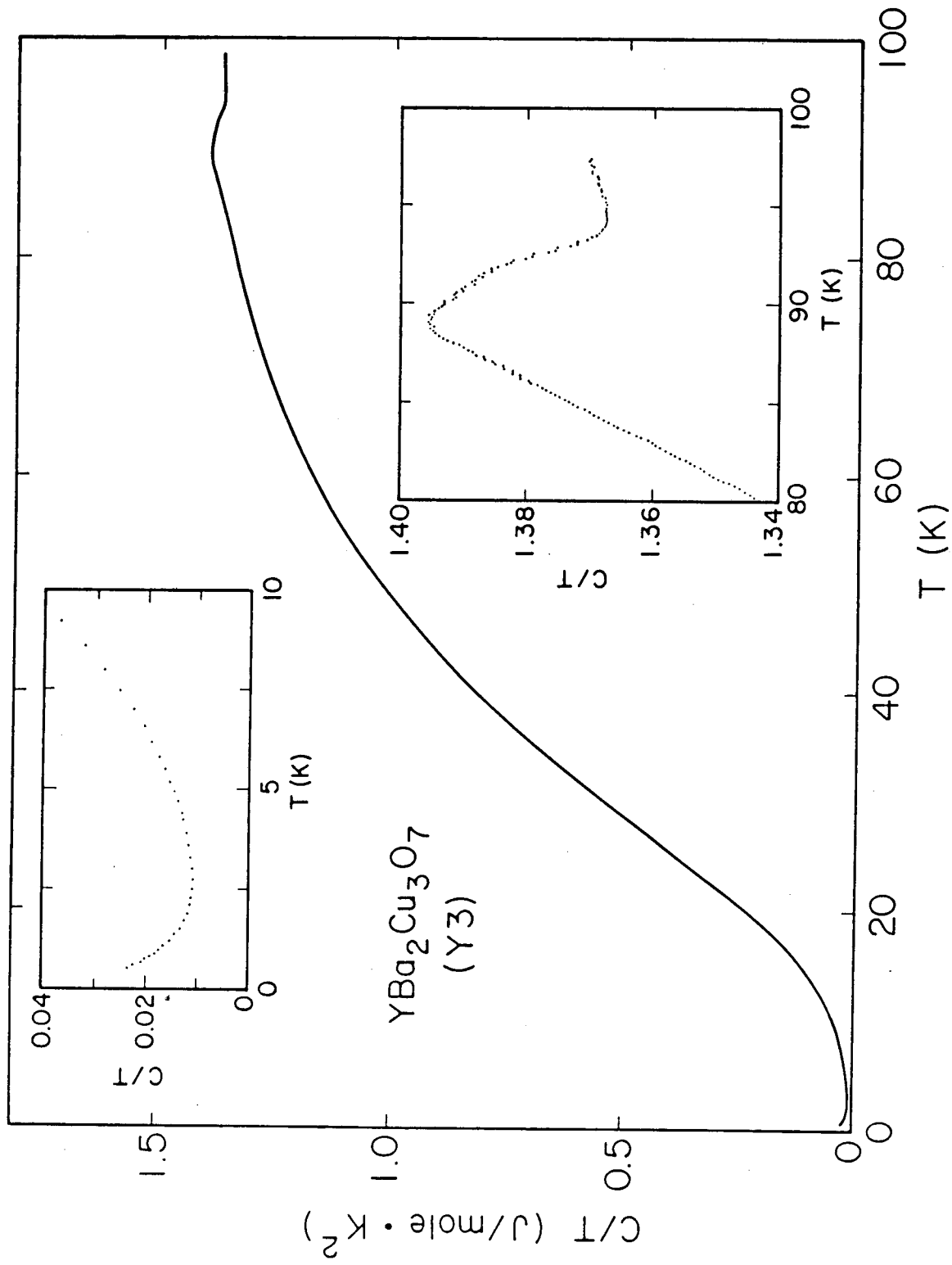
$T_c$	H	$C_i(0)$	$\gamma(0)$	$\Delta C/T_c$	$\gamma$	$\theta_D$	Ref.
94	0	+	3.5	39±8	27±6	378	7,8
92	0,12	+	4.2			390	4
94	0	0	7.3			434	9
96	0			55	38		10
90	0,0.22	+	-8	53	37		11
93	0			22	15		12
93	0	+	0	46	32		13,14
94	0			42	29		14(a)
79	0,8		7.8	-26	-18	384	15
93	0,8	+	-12	69±15	48±10	380	16,17
92	0			33±16	23±4	400	18
92	0			37	26		19-21
89	0	0	-9			420	5(b)
92	0	+	11.4				22
89	0			16±3	11±2		2(b)
90	0-6			42±2	29±1		2,23(b)
91	0			43±7	30±5		24
91	0			44±11	31±8		25
90	0			40±3	28±2		26
92	0			59	41		27
94	0,5	+	5.5±0.5	48±2	34±1	389	28,29
94	0	+	8.21			383	30,31
91	0	+	12			390	32(c)
91	0	+	19			371	32(c)
91	0	+	20			368	32(c)
92	0-7	+	6.95	47	33	457	(d)
92	0-7	+	6.8	52	36	452	(d)

(a) Gd substituted for Y.

(b) Single crystal.

(c) Three samples made by oxalate coprecipitation, solid state and organometallic precursor decomposition, respectively.  $\gamma(0)$  for a thick film was 73 and for a powdered sample 34. For a sample which was not superconducting above 70K  $\gamma(0)=53$ .

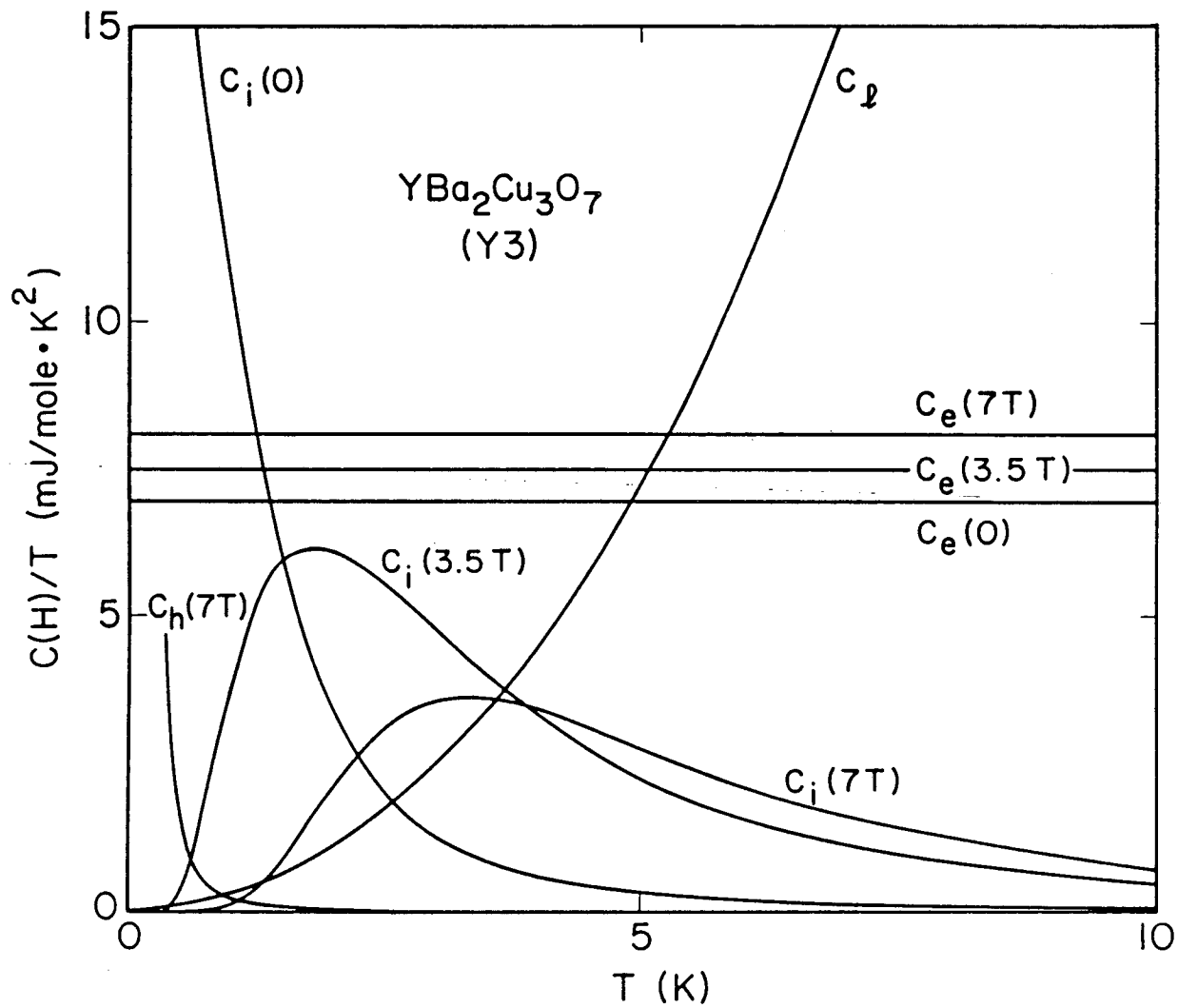
(d) This research.



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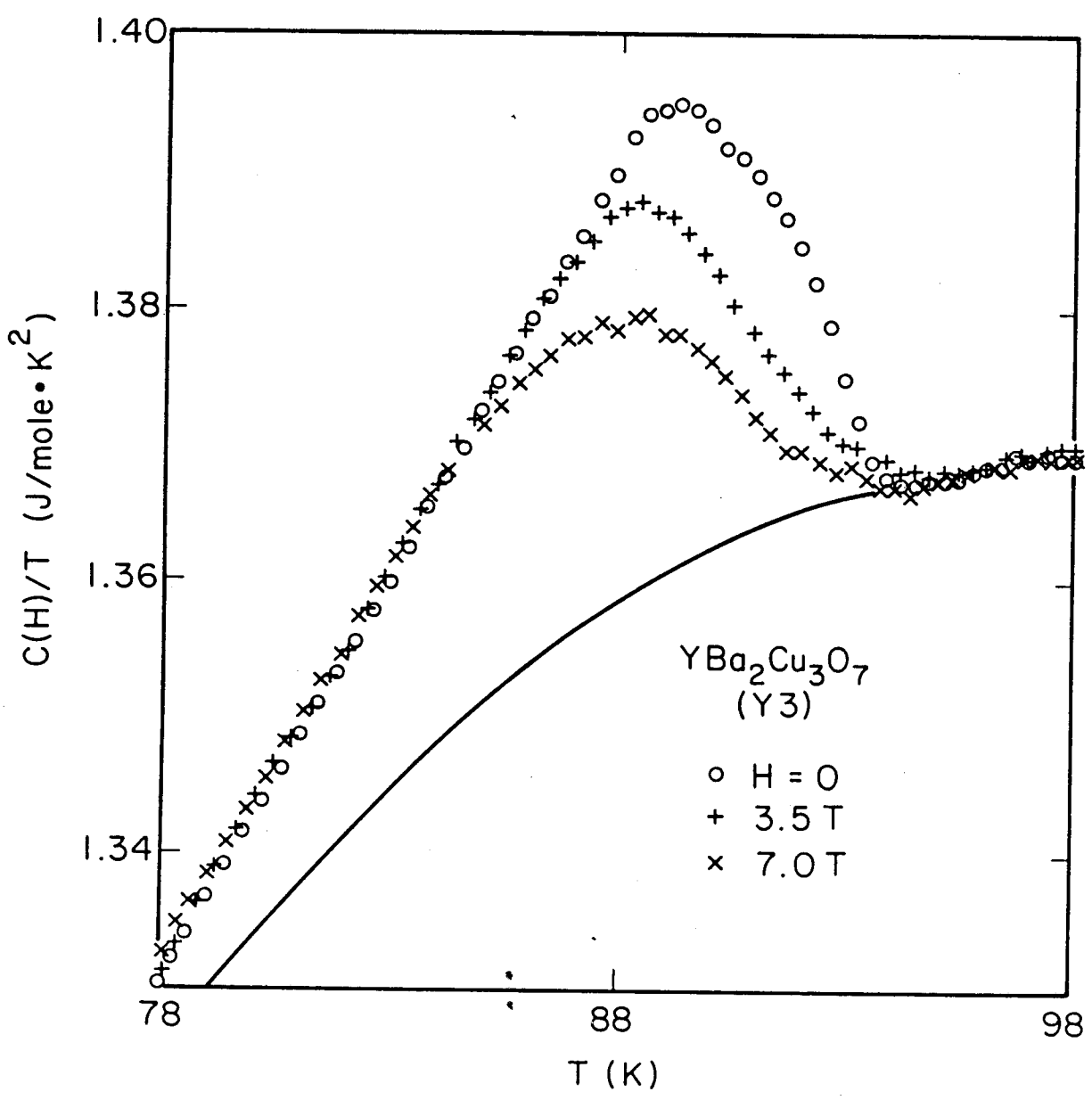
Figure 1. C/T vs T for Y3.





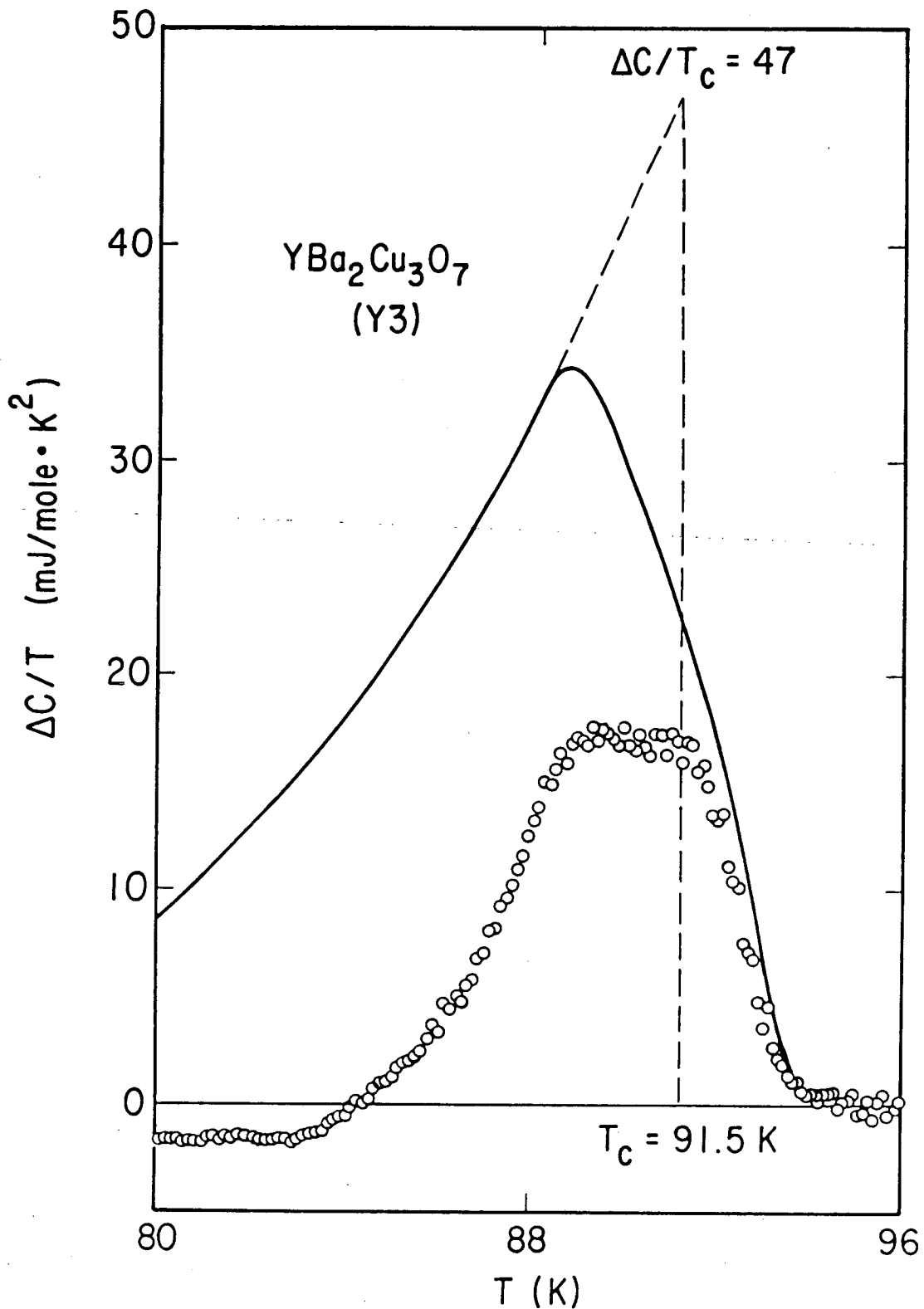
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Figure 2. Analysis of C for Y3 into component contributions.



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Figure 3. Field dependence of  $C$  for Y3 near  $T_c$ . The solid curve represents the field-independent data for Y3.



XBL 882-492

Figure 4. Estimation of  $\Delta C(T_c)$  for Y3. The solid curve represents the difference between the zero-field data and the data for Y5 (see Fig. 3). The dashed curve is the entropy conserving estimate of  $\Delta C$ . The open circles give, for comparison,  $[C(H=0) - C(7T)]/T$ .

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