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OF SOME HIGH-T<sub>c</sub> \*

N.E. Phillips, R.A. Fisher, S.E. Lacy, C. Marcenat,  
J.A. Olsen, W.K. Ham, A.M. Stacy

Materials and Chemical Sciences Division  
Lawrence Berkeley Laboratory  
University of California  
Berkeley, CA 94720

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# MAGNETIC FIELD DEPENDENCE OF THE SPECIFIC HEAT OF SOME HIGH- $T_c$ SUPERCONDUCTORS\*

N. E. Phillips, R. A. Fisher, S. E. Lacy, C. Marcenat, J. A. Olsen, W. K. Ham and A. M. Stacy

Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720 U.S.A.

The specific heats,  $C$ , of 5 samples of  $La_{1.85}M_{0.15}CuO_{4-y}$  ( $M=Ca, Sr, Ba$ ), one sample of  $La_2CuO_{4-y}$ , and one sample of  $YBa_2Cu_3O_{9-y}$  have been measured between 0.4 and 40K, in magnetic fields,  $H$ , to 7T. For the  $La_{1.85}M_{0.15}CuO_{4-y}$  samples the  $H$  dependence of  $C$  near  $T_c$  and near 1K, where  $C$  is dominated by the electronic contribution, gives information about the fraction of the sample that is a bulk superconductor and the density of electronic states. The fraction of bulk superconductivity indicated by the Meissner effect does not correlate well with that indicated by  $C$ .  $La_2CuO_{4-y}$  has a linear term in  $C$ , in qualitative agreement with a theoretical prediction [1].

Measurements of specific heat were made on samples of  $La_2CuO_{4-y}$  (La1),  $La_{1.85}M_{0.15}CuO_{4-y}$  (Ca1, Sr1, Sr2, Ba1 and Ba2) and  $YBa_2Cu_3O_{9-y}$  (Y1). Meissner effect measurements were made in 12.5G. The high-temperature onset of a change in magnetic susceptibility,  $\chi$ , was taken as  $T_c$ , and the transition width,  $\Delta T_c$ , as the temperature interval of the 10-90% change in  $\chi$ . Calculation of the fractional Meissner effect,  $-4\pi\chi_V$ , was based on the total sample volume. Two germanium thermometers were used for the specific heat measurements, a standard 0.3< $T$ <40K thermometer and a high-resolution one for 2.5< $T$ <40K which was used only for Ca1 and Sr2. The precision of the total measured  $C$  was 0.1% or 0.01% depending on the thermometer. Samples La1, Ca1, Sr2, Ba2 and Y1 were about 25g, and Ba1 and Sr1 only 5g. For the former samples,  $C$  ranged from 30 to 60% of the total measured. Parameters characterizing the samples are given in Table I.

In the following discussion and analysis of the data, subscripts are used to distinguish the various components of  $C$ :  $e$  for electronic,  $l$  for lattice,  $h$  for hyperfine, and  $i$  for impurity; additional subscripts  $n$ ,  $s$ , and  $m$  are used to distinguish the normal, superconducting and mixed states; and a quantity in parentheses following the symbol for a component of  $C$  or for the coefficient of one of its terms specifies the value of  $H$ . Even for  $H=0$ , all samples show a linear term in  $C$ ,  $\gamma(0)T$ , which is taken to be  $C_e$  for a fraction of the sample,  $1-f_s$ , that is not superconducting. One expects  $C_l$  to be independent of  $H$ , and  $C_l = B_1T + B_2T^3$  in the low-temperature limit. In the mixed state there are field-dependent terms in  $T$  and  $T^3$  for  $C_e$ ;  $C_{em} = \gamma(H)T + B_3(H)T^3$  [2]. For  $H \neq 0$  a hyperfine specific heat,  $C_h = A(H)/T^2$  is expected. However, for  $H=0$  most samples show deviations from the expected low-temperature limiting behavior,  $C = C_e + C_l = \gamma(H)T + [B_1 + B_3(H)]T^3$ , of the form  $A(0)/T^2$ . These deviations are apparently associated with a magnetic "impurity" that becomes partially ordered for  $0.4 < T < 1K$ . The evidence for this is clearest for the sample Sr2 for which Schottky anomalies with characteristic temperatures proportional to  $H$  are apparent for  $H=7T$  and particularly for  $H=3.5T$ . The results for all other samples of the La-based compounds are consistent with amounts of the same impurity that vary from sample to sample in proportion to

the observed value of  $A(0)$ . The experimental values of  $A(H)$  are then accounted for by the sum of the impurity contributions,  $A(0)/T^2$ , for that fraction of the sample not penetrated by flux and the hyperfine contribution,  $A(H)/T^2$ , calculated for the interaction of H with the nuclear moments for that part of the sample penetrated by flux, the penetration being measured by  $\gamma(H)$ .

For sample Sr2, the analysis of C into its components for  $T < 10K$  is represented in Fig. 1. For Ca2, Sr2 and La1, the only samples that show a measurable dependence of  $C_e$  on H, the field dependence is illustrated in Fig. 2. Within the precision of the data  $C_2$  is nearly the same for all the La-based compounds. It is shown as  $C_2/T^3$  for sample Ca1 in Fig. 3. Parameters derived from these analyses are listed in Table I for all the La-based samples. Fig. 4 shows  $[C_e(0) - C_e(7T)]/T$  for Ca1 and Sr2. The low-temperature behavior is in qualitative agreement with expectation for the mixed state in  $H=7T$ ; the dashed lines represent entropy conserving constructions used to estimate  $\Delta C$  at  $T_c$ .

If a fraction  $f_s$  of the sample is superconducting,  $\Delta C = 8f_s \gamma T_c$  and  $\gamma(0) = (1 - f_s)\gamma$ , where  $\beta$  is a numerical coefficient equal to 1.43 in the weak coupling limit,  $\gamma$  is the coefficient of  $C_e$  for the whole sample and  $\gamma(0)$  is the value measured in zero field. If  $\beta = 1.43$  is assumed, these two relations can be solved to obtain: for Ca1,  $f_s = 0.31$  and  $\gamma = 4.4 \text{ mJ/mole} \cdot K^2$ ; for Sr2,  $f_s = 0.82$  and  $\gamma = 8.6 \text{ mJ/mole} \cdot K^2$ . Empirically,  $\gamma(H)$  is approximately linear in H for  $H_{c1} < H < H_{c2}$  [3]. With this approximation  $H_{c2}$  at 0K, extrapolated from  $\gamma(7T)$  is 39T for Ca1 and 65T for Sr2. These values are in quite reasonable agreement with reported values [4] but there is enough latitude to allow  $\beta = 2$ . Other interesting results include the poor correlation of  $f_s$  obtained in this way for Ca1 and Sr2 with the Meissner effect, the obvious discrepancy between the field independent  $\gamma$  values and Meissner effect data for other samples, the nonzero value of  $\gamma$  for  $La_2CuO_{4-y}$ , which is predicted theoretically [1], and its strong field dependence. For  $La_{2-x}Sr_xCuO_{4-y}$  other measurements of  $C(0)$  and  $\Delta C/T_c$  have been reported [5].

For the Y-based compound, as shown in Fig. 5, analysis of the data is complicated by a large impurity effect. However, rough estimates of  $\gamma(0)$ ,  $\partial\gamma(H)/\partial H$ , and  $\theta_D$  are included in Table I.

## REFERENCES

\*Work supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

- 1) P. W. Anderson, preprint.
- 2) K. Maki, Phys. Rev. **A3**, 702 (1965).
- 3) cf.: G.R. Stewart and B.L. Brandt, Phys. Rev. **B29**, 3908 (1984); J.F. DaSilva, N.W.J. Van Duykern and Z. Dokoupil, Physica **32**, 1253 (1966); R. Radebaugh and P.H. Keesom, Phys. Rev. **149**, 217 (1966); F.J. Morin, J.P. Maita, H.J. Williams, R.C. Sherwood, J.H. Wernick and J.E. Kunzler, Phys. Rev. Lett. **8**, 275 (1962).
- 4) cf.: T.P. Orlando, K.A. Delin, S. Foner, E.J. McNiff, Jr., J.M. Tarascon, L. H. Greene, W.R. McKinnon and G.W. Hull, Phys. Rev. **B35**, 5347 (1987); D.K. Finnemore, R.N. Shelton, J.R. Clem, R.W.

## REFERENCES (continued)

- McCallum, H.C. Ku, R.E. McCarley, S.C. Chen, P. Klavins and V. Kagan, Phys. Rev. **B35**, 5319 (1987).
- 5) B. Batlogg, A.P. Ramirez, R.J. Cava, R.B. van Dover and E.A. Rietman, Phys. Rev. **B35**, 5340 (1987); B.D. Dunlap, M.V. Nevitt, M. Sloski, T.E. Klippert, Z. Sungoila, A.G. McKale, D.W. Capone, R.B. Poeppel and B.K. Flandermeyer, preprint; M. Decroux, A. Junod, A. Bezingue, D. Cattani, J. Cors, J.L. Jorda, A. Stettler, M. Francois, K. Yvon, O. Fischer and J. Muller, preprint.

Table I. Parameters characterizing the high- $T_c$  superconductors  $\text{La}_{1.85}\text{M}_{0.15}\text{CuO}_{4-y}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$ . (All units are in mJ, mole, K and T. ND = not determined.)

Sample	$-4\pi\chi_V$	$T_c(\text{K})$	$\Delta T_c(\text{K})$	$\rho/\rho_0$	$A(0)$	$\gamma(0)$	$\partial\gamma(H)/\partial H$	$B_3(0)$	$\partial B_3'(H)/\partial H$	$B_5$	$\Theta_D(\text{K})$
La1	-	-	-	0.8	0.16	1.10	-0.096	0.137	0	0.0019	460
Ca1	0.26	22	6	0.8	<0.02	3.05	0.035	0.145	0.0019	0.0013	450
Sr1	0.20	37	18	0.7	~0	3.9	~0	0.15	~0	ND	450
Sr2	0.35	37	8	0.7	0.16	1.54	0.109	0.168	0.0011	0.00085	430
Ba1	0.24	33	11	0.75	0.34	3.6	~0	0.16	~0	ND	440
Ba2	ND	34	>30	0.75	0.36	3.6	~0	0.16	~0	0.0013	440
Y1	0.25	91	9	0.6	~4400	20	0.6	0.47	ND	0.0006	380

## FIGURE CAPTIONS

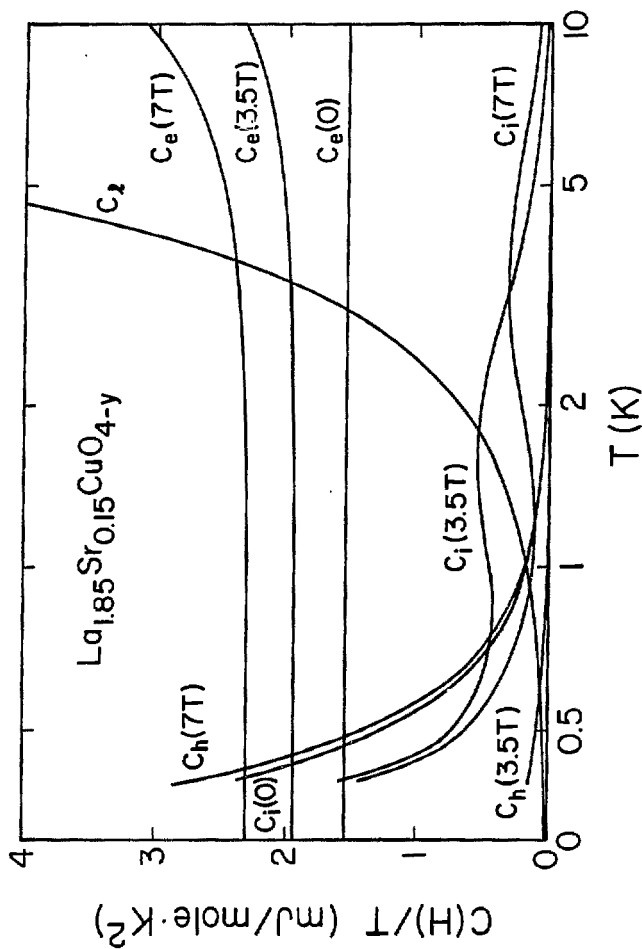
Fig. 1. Components of C for  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4-y}$ .

Fig. 2.  $(C_e + C_2)/T$  vs T for  $\text{La}_{1.85}\text{M}_{0.15}\text{CuO}_{4-y}$ .

Fig. 3.  $C_1$  for  $\text{La}_{1.85}\text{Ca}_{0.15}\text{CuO}_{4-y}$  vs T.

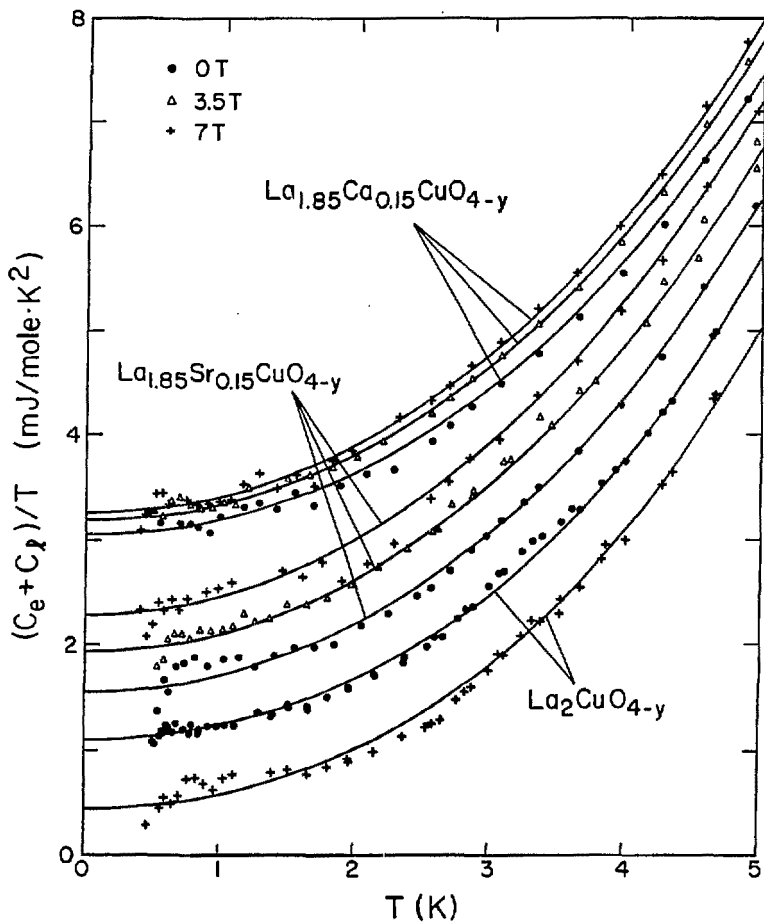
Fig. 4.  $[C(0)-C(7)]/T$  vs T for  $\text{La}_{1.85}\text{M}_{0.15}\text{Cu}_{4-y}$ .

Fig. 5. C/T vs T for  $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$  at 0 and 7.5T.



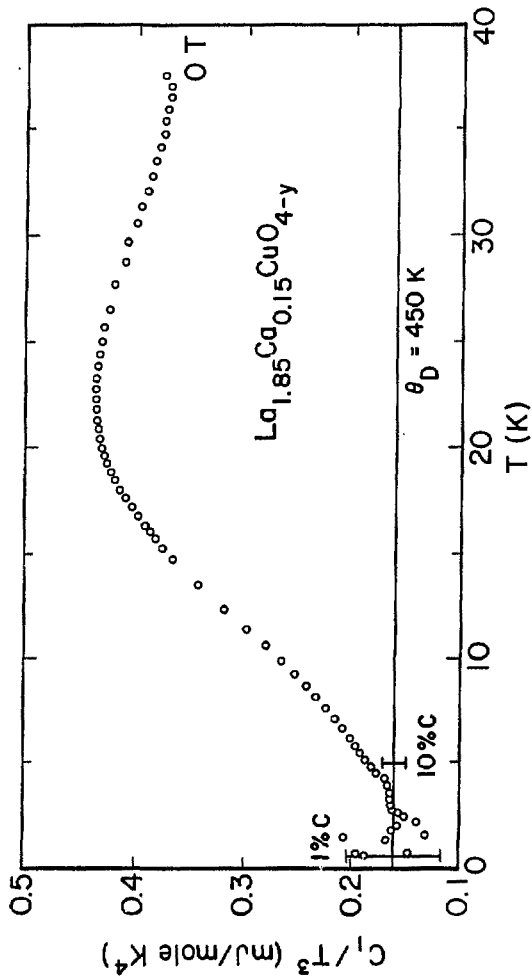
XBL 875-2028

FIGURE 1



XBL 875-2033

FIGURE 2



XBL 875-2282

FIGURE 3

XBL 875-2027B

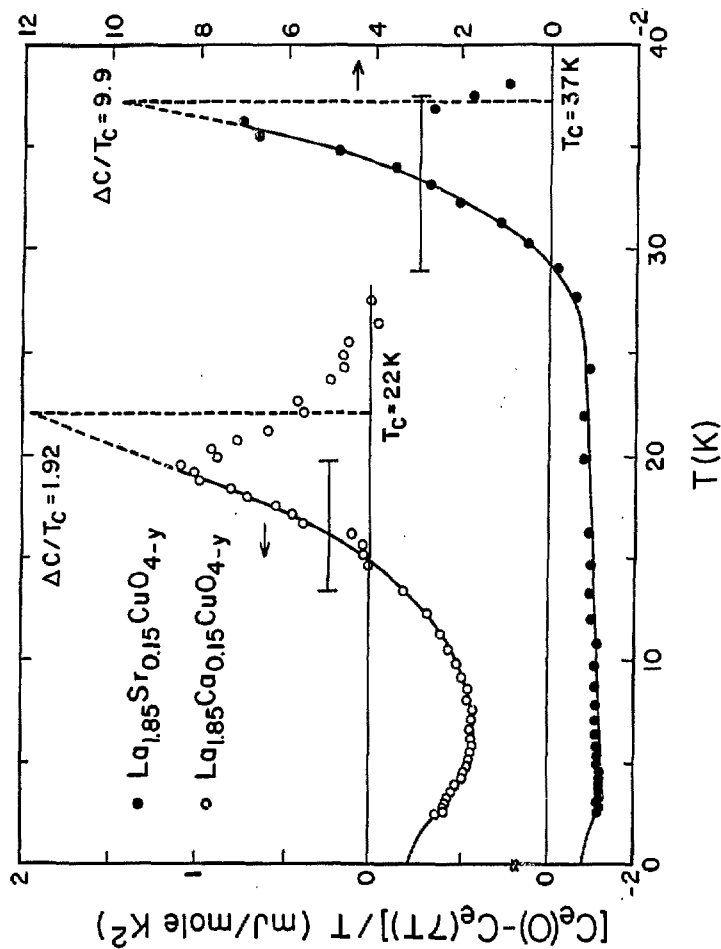
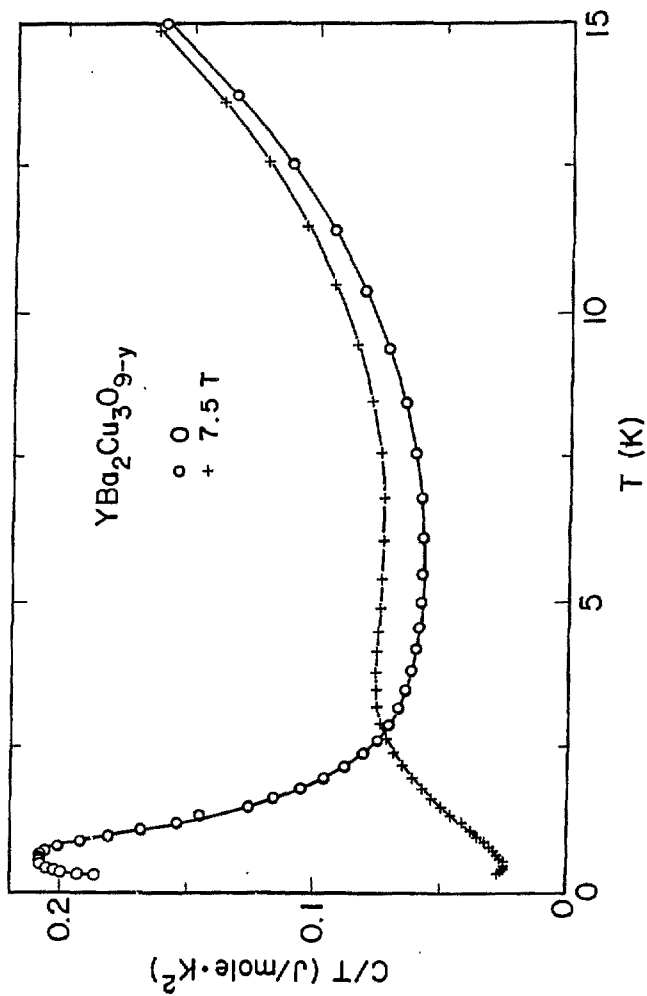


FIGURE 4





XBL 875-2151

FIGURE 5