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Specific-heat measurements on superconducting Bi-Ca-Sr-Cu and Tl-Ca-Ba-Cu oxides: Absence of a linear term in the specific heat of Bi-Ca-Sr-Cu oxides

R. A. Fisher, S. Kim, S. E. Lacy, and N. E. Phillips
Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

D. E. Morris, A. G. Markelz, and J. Y. T. Wei
Physics Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

D. S. Ginley
Sandia National Laboratory, Albuquerque, New Mexico 87185
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Specific-heat data, extending from 0.4 to 120 K, in both a zero field and at 7 T, are reported for five samples of Bi-Ca-Sr-Cu oxide and one of Tl-Ca-Ba-Cu oxide. The occurrence of bulk superconductivity in all six samples is shown by Meissner-effect measurements, and confirmed for the Tl sample and two Bi samples by the specific-heat data. In a zero field, the Tl sample shows a contribution to the specific heat that is linear in temperature and comparable to those reported for $YBa_2Cu_3O_7$. For all samples of the Bi compound the linear term is zero within the experimental uncertainty, and is at least an order of magnitude smaller.

One of the most striking properties of the new high-T_c oxide superconductors[1,2] is the occurrence in a zero magnetic field of a linear term[3] $\gamma(0)T$ in the specific heat (C). This term is well known from measurements on the La-Cu oxides and especially from measurements on $YBa_2Cu_3O_7$ which has been studied more extensively. Since a linear term is generally associated with the normal state and is expected to disappear in a zero field, i.e., in the fully superconducting state, there has been considerable interest in the origin of this term. An incomplete transition to the superconducting state,[4] the presence[5] of two-level systems (TLS), and the presence of impurity phases,[6-8] have all been noted as possibilities. However, the most intriguing interpretation, and one suggested both by the generality of the occurrence of the linear term and by the relative consistency[9] of $\gamma(0)$ values for different Y-Ba-Cu-O samples, is that it is an intrinsic property of the superconducting state and a manifestation of a different kind of superconductivity such as that predicted for the resonant-valence-bond (RVB) model.[10] The discovery of the new Bi- (Ref. 11) and Tl-containing[12] copper-oxide superconductors provides an opportunity to test further the generality of the zero-field linear term. We report here specific-heat measurements on five samples of Bi-Ca-Sr-Cu oxide and one of Tl-Ca-Ba-Cu oxide all of which are bulk superconductors. For the Tl-Ca-Ba-Cu-O sample, $\gamma(0)\neq 0$ and has a value of the same order of magnitude as those[9] for Y-Ba-Cu-O but for each of the Bi-Ca-Sr-Cu-O samples, two of which contain two superconducting phases, $\gamma(0)=0$ within the experimental uncertainty, and is at least an order of magnitude smaller than typical values for Y-Ba-Cu-O. Thus, a nonzero zero-field linear term of the magnitude observed in La-Cu-O and Y-Ba-Cu-O is not a general property of the high-T_c superconducting oxides.

Samples 1, 3, and 4 of Bi-Ca-Sr-Cu-O were prepared by solid-state reaction of the oxides or carbonates (99.999 wt.% purity except 99 for $SrCO_3$). Disks were pressed and fired in air on gold foil, at 850 °C for 1 h for sample 1, at 800 °C for 24 h followed by 24 h at 870 °C for sample 3, and at 800 °C for 24 h followed by 50 h at 870 °C for sample 4. The reacted material was ground, mixed, sieved, and repressed into ~10-g disks. Samples 2 and 5 of Bi-Ca-Sr-Cu-O and the Tl-Ca-Ba-Cu-O sample were prepared by solid-state reaction of the oxides (≥ 99.9 wt.% purity). Disks were pressed and fired in air in a Pt vessel, at 850 °C for 4 h for BCS-2 and BCS-5 and for 0.5 h for TCB-1. The superconducting transitions were characterized by measurements of the volume magnetic susceptibility (χ_v) on cooling in a magnetic field (H) of 8 Oe (i.e., the Meissner effect), and examples of the results are shown in Fig. 1. The values of T_c (onset) and ΔT_c (10–90% width) and the maximum values of $-4\pi\chi_v$ (the fractional Meissner effect) are given in Table I.

The results for the Tl sample conform to those for the earlier oxide superconductors and, together with those for Y-Ba-Cu-O, they provide a basis for comparison for the

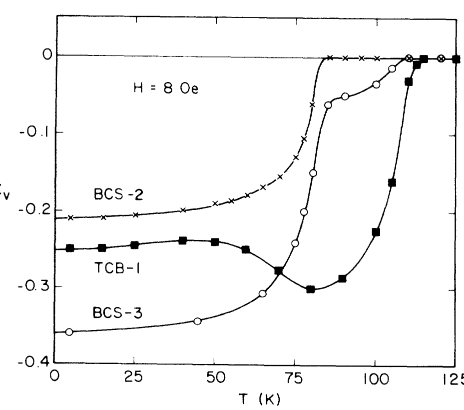

FIG. 1. Typical Meissner-effect data for the specific-heat samples.

TABLE I. Properties of the samples. Units are mJ, mol, K, and T. T_c and ΔT_c are from Meissner-effect measurements. Samples BCS-3 and BCS-4 show two transitions, for which T_c, ΔT_c, and $-4\pi\chi_v$ are listed separately. n_i is the number of moles of magnetic impurity per mole of sample determined from the entropy of the Schottky-type specific-heat anomaly in 7 T (spin $\frac{1}{2}$ assumed).

Sample	Starting composition	T_c	ΔT_c	$-4\pi\chi_v$	$(\Delta C/T)_{max}$	B_3	$\gamma(0)$	n_i
TCB-1	$TlCaBaCu_2O_{5.5}$	114	~20	0.30	5	1.06	16	0.052
BCS-1	$Bi_{2.15}Ca_{1.17}Sr_{1.68}Cu_2O_8$	80	~20	0.12	. . . [a]	2.47	0	0.017
BCS-2	$Bi_2CaSr_2Cu_2O_8$	84	~30	0.21	. . . [a]	1.82	0	0.012
BCS-3	$Bi_2Ca_2Sr_2Cu_4O_{11}$	110 95	~10 ~30	0.04 0.34	16	2.63	0	0.058
BCS-4	$Bi_2Ca_6Sr_2Cu_8O_{19}$	110 80	~20 ~35	0.09 0.13	. . . [a]	2.85	0	0.064
BCS-5	$Bi_2CaSr_2Cu_2O_8$	84			. . . [a]	1.74	0	0.013

[a]Transition was too broad or too small to permit an estimate.

Bi samples. The data for $H=0$ and 7 T and $T\leq 10$ K are shown in Fig. 2. For $H=0$ there is an upturn in C/T at the lowest temperatures, which indicates the existence of an anomaly at a temperature well below 1 K. For $H=7$ T the anomaly is shifted to the vicinity of 3.5 K. These anomalies, associated with the presence of magnetic impurities, are well within the range observed for Y-Ba-Cu-O samples. The data for $H=0$ and $3\leq T\leq 12$ K were fitted by the five-parameter expression

$$C=A_{-3}T^{-3}+A_{-2}T^{-2}+\gamma(0)T+B_3T^3+B_5T^5\,, \quad (1)$$

where the A_{-3} and A_{-2} terms represent the upturn in C/T and the T^3 and T^5 terms are the first two terms in the low-temperature expansion of the lattice specific heat (C_l). The least-squares fit gave $\gamma(0)=16$ mJ/mol K^2, and an rms deviation from the experimental data of 0.6%. Omission of the $\gamma(0)T$ term from the fitting expression increased the rms deviation to 2.0%. When applied to the data for the five low-impurity Y-Ba-Cu-O samples that have been studied in this laboratory, the same fitting procedure gave $\gamma(0)=6.8$, 6.9, 7.9, 7.0, and 7.0 mJ/mol K^2, and rms deviations of 0.4, 0.7, 0.4, 0.9, and 1.0%. The rms deviations increased to 4.2, 4.7, 4.7, 5.3, and 6.0% with omission of the $\gamma(0)T$ term. [The difference in the effects of omission of the $\gamma(0)T$ term on the rms deviations for the Tl and Bi samples is related to the relative magnitude of $\gamma(0)$ and B_3—see Table I.]

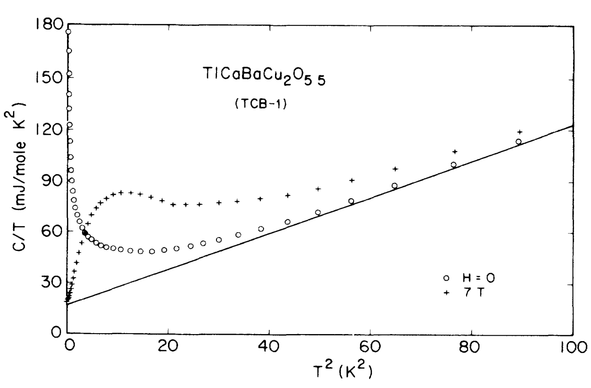

FIG. 2 C/T vs T^2 for TCB-1 for $T\leq 10$ K and $H=0$ for 7 T. The straight line represents the T and T^3 terms of the least-squares fit to the zero-field data.

The uniqueness of the values of $\gamma(0)$ and B_3 derived from these fits, and those described below for the Bi samples, is attested by the fact that they, and the rms deviations, are not sensitive to reductions in the temperature interval of the fit, to reasonable changes in the form of the expression used to fit the upturn in C/T (e.g., the high-temperature tail of a Schottky anomaly in place of $A_{-3}T^{-3}+A_{-2}T^{-2}$), nor, if higher-order terms in C_l are included in the fitting expression, to extension of the interval of the fit to higher temperatures. (The interval of the fit cannot be extended to lower temperatures without either introducing a substantial complication into the fitting expression used for the upturn or accepting a substantial reduction in quality of the fit, as would be expected for an upturn produced by interimpurity interactions. Neither the Schottky-anomaly-like tails nor the T^5 terms are uniquely determined by the fits.)

The data for the same Tl sample near T_c (see Fig. 3) show a broad superconducting transition. The breadth of the transition should not affect conclusions based on the values of the parameters derived from the low-temperature data, but it does complicate an estimate of $\Delta C(T_c)$ for the ideal sharp transition. However, the maximum observed value of $\Delta C/T\equiv[C(0)-C(7\text{ T})]/T$, given in Table I, is certainly a lower limit for the ideal value and is probably smaller by a factor of 2 to 3 (see, e.g., Ref. 9).

The Bi samples show the same evidence of magnetic impurities as the Tl sample and typical Y-Ba-Cu-O samples, as illustrated in Fig. 4 by data for BCS-1. For BCS-3 and BCS-4 the impurity concentrations are similar to, but higher than, that of the Tl sample, but for BCS-1, BCS-2, and BCS-5 their concentrations are substantially lower (see Table I). The straight line in Fig. 4, and that in Fig. 2, represent the correct values of $\gamma(0)T+B_3T^3$ for the $H=0$ data, those obtained by the analytical fit, which properly takes into account the other terms in Eq. (1). [It is important to note that an attempt to determine $\gamma(0)$ and B_3 by visually fitting a straight line to the data cannot be expected to give the correct values.] The value of $d\gamma/dH$ for the Bi samples is ~0.15 mJ/mol K^2T.

For *all* the Bi samples the zero-field data between 3 and

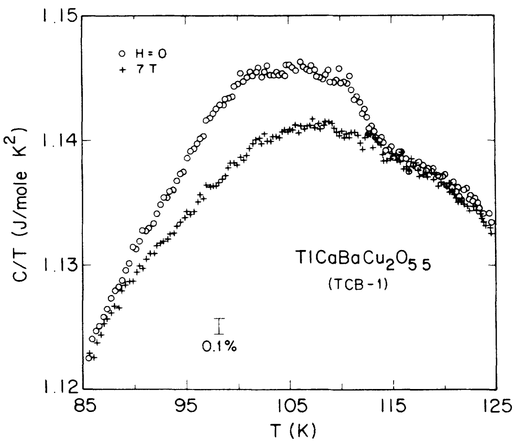

FIG. 3. C/T vs T for TCB-1 in the region of T_c for $H=0$ and 7 T.

12 K are well represented by Eq. (1) *without the linear term*. The rms deviations are 0.9, 1.0, 0.4, 0.4, and 1.1 %. Inclusion of a linear term in the fitting expression gives small, and variable, values of $\gamma(0)$ that are at the limit of sensitivity of the measurement: $\gamma(0)=-1.0$, 1.0, 0.4, 1.0, and 1.0 mJ/mol K^2. Furthermore, the fit is not improved—the rms deviations are essentially unchanged. In this respect, the data for Bi-Ca-Sr-Cu-O differ conspicuously from those for Tl-Ca-Ba-Cu-O and Y-Ba-Cu-O, and preclude the existence of a linear term that is not an order-of-magnitude smaller than that commonly observed in Y-Ba-Cu-O, for both the "$T_c=120$ K" and "$T_c=90$ K" phases. Another test of this conclusion, based on use of the same fitting expression but with various *fixed* values of $\gamma(0)$, is shown in Fig. 5: Minimum values of the rms deviations are obtained for $-0.5<\gamma(0)<0.5$ mJ/mol K^2. A third test is afforded by *adding* a linear term $\gamma'(0)T$ to the experimental data and refitting with Eq. (1). For $\gamma'(0)=7$ mJ/mol K^2, approximately that value is recovered when the linear term is included in the fitting expression; without the linear term in the fitting expression the rms deviations increase by factors of 2–3. For the temperature interval of the fit by Eq. (1), the zero-field data with the T^{-3} and T^{-2} terms subtracted out are

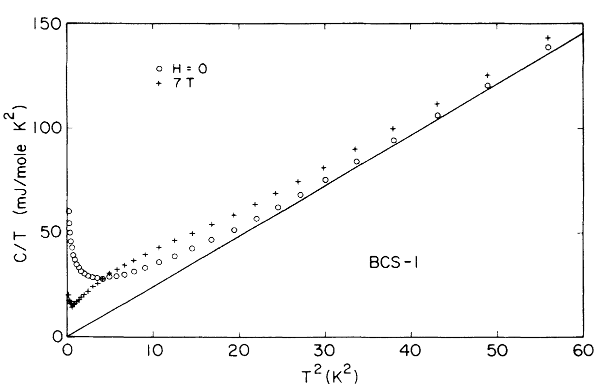

FIG. 4. C/T vs T^2 for BCS-1, for $T \leq 8$ K, in both zero field and 7 T. The straight line represents the T and T^3 term of the least-squares fit to the zero-field data.

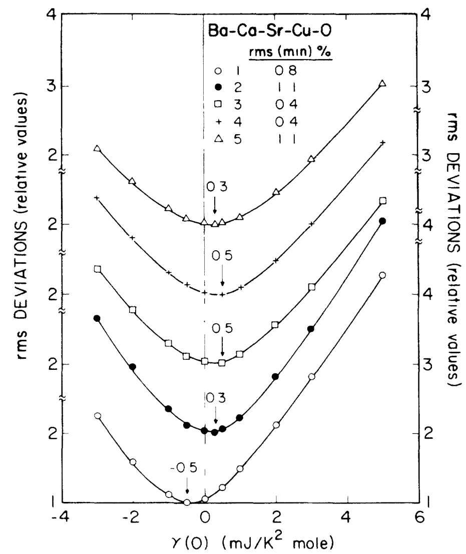

FIG. 5. Ratios of the rms deviations to the minimum values, obtained by fitting with Eq. (1) and fixed values of $\gamma(0)$, for various values of $\gamma(0)$.

shown in Fig. 6 for four of the Bi samples and for the Tl sample. The solid lines represent B_3T^3 for the Bi samples and $\gamma(0)T+B_3T^3$ for the Tl sample.

Among the Bi samples, an anomaly at T_c was observed only for BCS-3 and BCS-4 (the samples that showed two magnetic transitions). For BCS-3, two relatively sharp transitions, which corresponded to the transitions found magnetically, were observed. They are illustrated as $\Delta C/T$ in Fig. 7, and the maximum observed value of

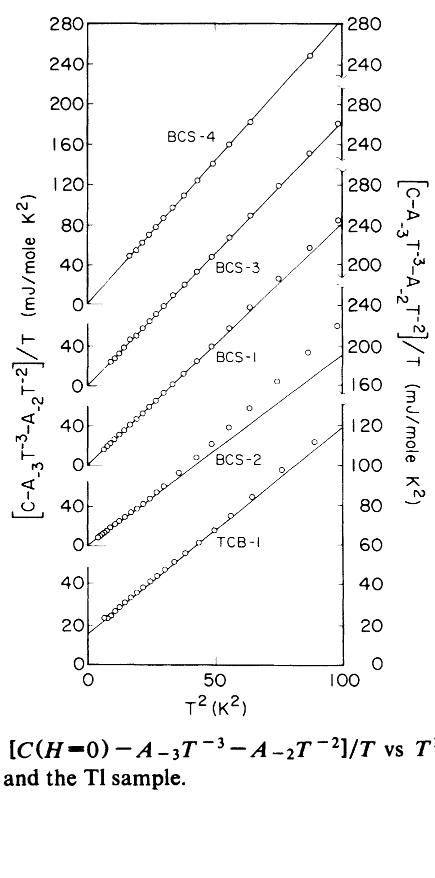

FIG. 6. $[C(H=0)-A_{-3}T^{-3}-A_{-2}T^{-2}]/T$ vs T^2 for four Bi samples and the Tl sample.

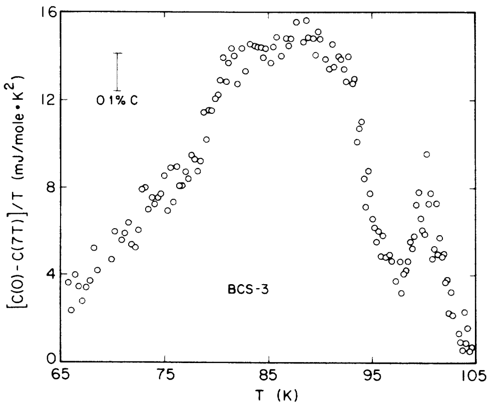

FIG. 7. $[C(H=0)-C(7T)]/T$ vs T for BCS-3 in the region of T_c.

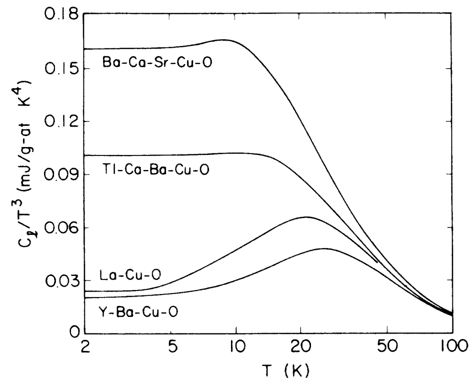

FIG. 8. Comparison of the lattice specific heat for La-Cu-O, Y-Ba-Cu-O, Tl-Ca-Ba-Cu-O, and Bi-Ca-Sr-Cu-O.

$\Delta C/T$ is listed in Table I. For BCS-4, the two transitions in C were broader, and coalesced into one. For BCS-1, BCS-2, and BCS-5, the magnetic data notwithstanding, the bulk transitions are apparently too broad to be observed in the C data.

The lattice specific heats of BCS-1 and TCB-1 are compared with those of Y-Ba-Cu-O and La-Cu-O in Fig. 8.

The major conclusion of this Rapid Communication, that any linear term in the specific heat of Bi-Ca-Sr-Cu-O is at least an order of magnitude smaller than those commonly reported for Y-Ba-Cu-O, suggests that the linear term may not be a general feature of the superconducting state of the new oxide superconductors. If this suggestion is borne out by further experiment, the implications for the nature of the superconductivity of these materials could be significant because the linear term, if it is really an intrinsic property of the superconducting state, is perhaps the most fundamental empirical difference between these materials and other superconductors. Another possibility is that the linear term *is* an intrinsic property of the superconducting state, but with a substantial variability from one material to another that might be accounted for[13] within the framework of the resonating-valence-bond (RVB) model.

If the linear term is *not* an intrinsic property of the superconducting state, the difference between the Bi and Tl samples may reinforce a clue to its origin[6–8] in the other materials that has been noted earlier: The fact that the linear term is present in the Tl sample, which contains Ba, but not in the Bi samples, which do not, is consistent with the suggestion that the linear term is associated with a Ba-Cu oxide impurity. In the same connection, it is interesting that samples of both Sr- and Ca-doped La-Cu-O also have smaller linear terms than similar Ba-doped samples, but the occurrence of the linear term in La-Cu-O has not been as thoroughly studied as in Y-Ba-Cu-O.

Finally, we note that the absence of a linear term in a Bi-Ca-Sr-Cu-O sample has also been reported by Kumagai and Nakamura.[14]

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[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).
[3]The first published reports were as follows: M. E. Reeves, T. A. Friedman, and D. M. Ginsberg, Phys. Rev. B **35**, 7207 (1987); B. D. Dunlap, M. V. Nevitt, M. Slaski, T. E. Klippert, Z. Sungaila, A. G. McKale, D. W. Capone II, R. B. Poeppel, and B. K. Flandermeyer, *ibid.* **35**, 7210 (1987); L. E. Wenger, J. T. Chen, G. W. Hunter, and E. M. Logothetis, *ibid.* **35**, 7213 (1987).
[4]N. E. Phillips, R. A. Fisher, S. E. Lacy, C. Marcenat, J. A. Olsen, W. K. Ham, and A. M. Stacy, in *Novel Superconductivity,* edited by S. A. Wolf and V. Kresin (Plenum, New York, 1987), p. 739.
[5]B. Golding, N. O. Birge, W. H. Haemmerle, R. J. Cava, and E. A. Rietman, Phys. Rev. B **36**, 5606 (1987).
[6]A. P. Ramirez, R. J. Cava, G. P. Espinosa, J. P. Remeika, B. Batlogg, S. Zahurak, and E. A. Rietman, Mater. Res. Soc. Symp. Proc. **99**, 459 (1987).
[7]R. Kuentzler, Y. Dossmann, S. Vilminot, and S. el Hadigui, Solid State Commun. **65**, 1529 (1988).
[8]D. Eckert, A. Junod, A. Bezinge, T. Graf, and J. Muller, J. Low Temp. Phys. (to be published).
[9]R. A. Fisher, J. E. Gordon, S. Kim, N. E. Phillips, and A. M. Stacy, Physica C **153-155**, 1092 (1988).
[10]P. W. Anderson, Science **235**, 1196 (1987).
[11]C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Phys. B **68**, 421 (1987); H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, J. Appl. Phys. Lett. Jpn. **27**, L209 (1988).
[12]Z. Z. Sheng and A. M. Hermann, Nature **332**, 55 (1988); **332**, 138 (1988).
[13]P. W. Anderson (private communication).
[14]K. Kumagai and Y. Nakamura, Physica C **152**, 286 (1988).