Title

Specific Heat of YBa{sub 2}Cu{sub 3}O{sub 7}: Volume Fraction of Superconductivity; Parameters Characteristic of the Ideal Superconducting State

Authors

Phillips, N.E.
Fisher, R.A.

Publication Date

1991-03-01

LBL-30435

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

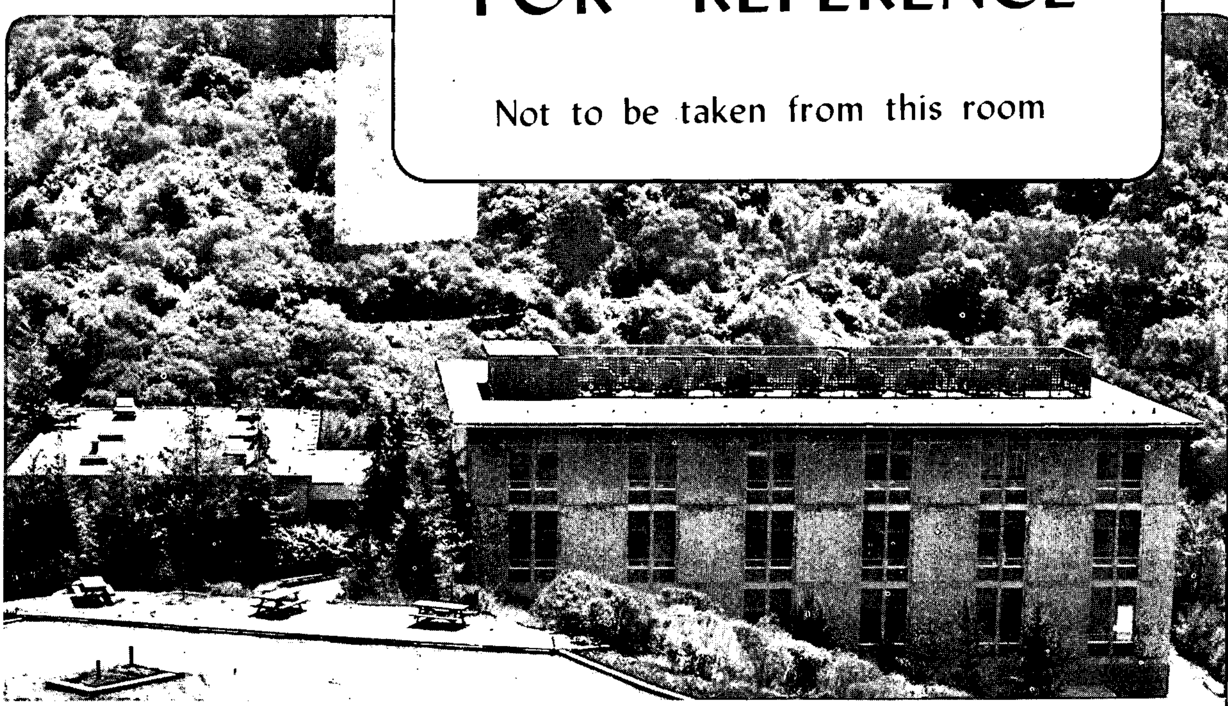
Materials & Chemical Sciences Division

Presented at the Electronic Structure and Mechanisms for High-T_c Superconductivity, Miami, Florida, January 3–9, 1991, and to be published in the Proceedings

Specific Heat of $YBa_2Cu_3O_7$: Volume Fraction of Superconductivity; Parameters Characteristic of the "Ideal" Superconducting State

N.E. Phillips and R.A. Fisher

March 1991



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

DISCLAIMER

SPECIFIC HEAT OF $YBa_2Cu_3O_7$: VOLUME FRACTION OF SUPERCONDUCTIVITY; PARAMETERS CHARACTERISTIC OF THE "IDEAL" SUPERCONDUCTING STATE

Norman E. Phillips and R.A. Fisher

Materials Sciences Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720, USA

January, 1991

Presented at the University of Miami Workshop on:
Electronic Structure and Mechanisms for
High Temperature Superconductivity
(3-9 January 1991)
Proceedings to be published by Plenum, N.Y.

This work was supported by the Director,
Office of Energy Research, Office of Basic Energy Sciences,
Material Sciences Division of the U.S. Department of Energy
under Contract No. DE-AC03-76SF00098.

SPECIFIC HEAT OF $YBa_2Cu_3O_7$: VOLUME FRACTION OF SUPERCONDUCTIVITY; PARAMETERS CHARACTERISTIC OF THE "IDEAL" SUPERCONDUCTING STATE

Norman E. Phillips and R.A. Fisher

Materials Sciences Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720, USA

INTRODUCTION

Experimentally determined parameters for $YBa_2Cu_3O_7$ (YBCO) are strongly sample dependent. However correlations among parameters derived from the specific heat (C) suggest that the variation reflects a variation in the volume fraction of superconductivity, (f_s). From these correlations f_s can be quantitatively determined and values of parameters characteristic of fully superconducting material can be derived. With additional assumptions, it is also possible to estimate the Sommerfeld constant (γ) for the fully normal state. Among the parameters of particular importance in establishing the correlations are the discontinuity in C [$\Delta C(T_c)$] at the critical temperature (T_c) and concentration (n_2) of localized Cu^{2+} magnetic moments. These are located on the YBCO lattice, at least in substantial measure, and are directly correlated with f_s. From an analysis of C in the vicinity of T_c it is possible to obtain information on the strength of the coupling responsible for the superconductivity; from a comparison of γ with that calculated for the bare density of states (γ_{bs}) the electron-phonon enhancement parameter (λ) can be obtained.

Some data for $(La_{2-x}Sr_x)CuO_4$ suggest similar correlations, but there are insufficient data for other high temperature superconductors (HTSC) to test this possibility.

The total specific heat of a YBCO sample that is reasonably typical of the better polycrystalline samples currently available is shown in Fig. 1. At T_c the lattice specific heat is large compared with the electronic contribution, and the feature associated with the transition to the superconducting state is only 3% of the total. Furthermore, there is no obvious discontinuity in specific heat. Comparison of data for different samples shows that a major part of the apparent breadth of the transition is associated with sample-to-sample differences, presumably inhomogeneities and other imperfections, but the nature of the specific-heat anomaly at T_c for an ideal sample has not yet been unambiguously established. For YBCO there can be inhomogeneities associated with oxygen stoichiometry and with the ordering of the O atoms. The inclusion of impurity phases probably also contributes to the breadth. The effect of small-scale defects of all kinds can be expected to be enhanced in HTSC relative to that in conventional superconductors because the coherence length (ξ) is smaller and is comparable to the lattice parameters. Furthermore, there is the expectation, also based on the small value of ξ, that fluctuation effects should be important in determining the shape of the specific-heat anomaly at T_c.

Figure 1 also shows the low-temperature "upturn" in C/T that is characteristic of virtually all samples of HTSC, at least those that have been studied below 1K. It is associated with electronic magnetic moments that order below 1K as shown by its magnetic-field dependence. After appropriate correction for the upturn there is still a non-zero intercept of C/T at T=0. This "linear term", $\gamma(0)T$, has attracted much attention. It was recognized very early (1) that it could be simply a manifestation of an incomplete transition to the superconducting state. However, independently of, and more or less simultaneously with, its experimental discovery (2), a linear term was predicted theoretically (3) as one of the consequences of the resonant valence bond (RVB) theory. In the RVB model the excitations from the superconducting ground state are qualitatively different from those in a conventional superconductor, and so is the thermodynamics. The development of an understanding of the origin of $\gamma(0)$ has, for these reasons, been a major goal of specific-heat measurements on HTSC.

ANALYSIS OF LOW-TEMPERATURE DATA

Empirically, at low temperatures the specific heat of the HTSC can be represented (4) as a sum of lattice (C_ℓ), hyperfine (C_h) and localized electronic magnetic moment (C_m) contributions, and the linear term (C_e). The latter is field dependent, $C_e = \gamma(H)T$. It is related to the normal state electronic specific heat, but

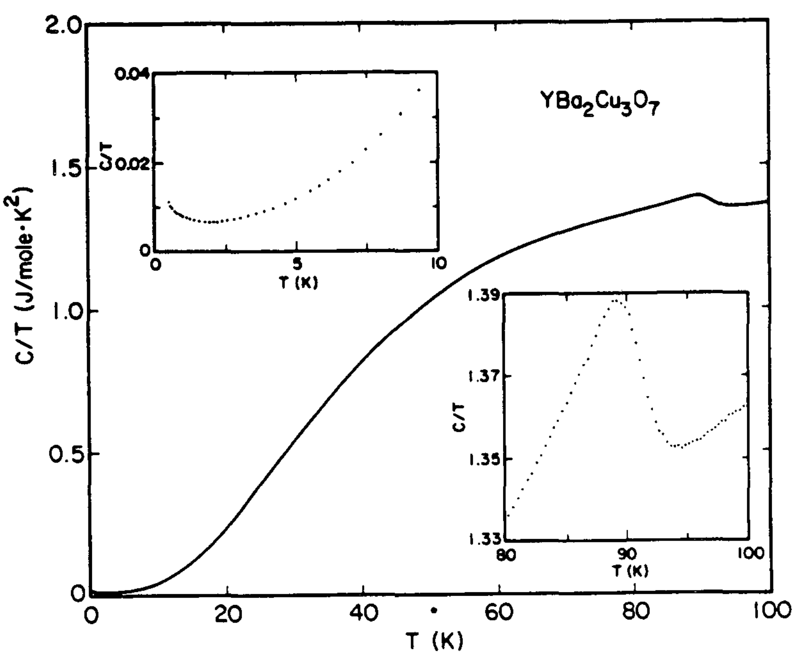


Figure 1. The total specific heat of a typical YBCO sample. The insets show actual data at low temperatures and in the vicinity of T_c

in many cases it includes other contributions. The lattice specific heat is independent of magnetic field (H) and is usually assumed to be the same in the normal and superconducting states. In the low-temperature limit the harmonic lattice expression for C_ℓ is $C_\ell = B_3 T^3 + B_5 T^5 + B_7 T^7 + \cdots$. In the temperature range of interest here, C_h is well represented by the lowest-order term in the high temperature expansion of a Schottky anomaly: $C_h = D(H)T^{-2}$. In the case of a nuclear magnetic moment interacting with the applied field $D(H) \propto H^2$, but this relation would not apply if electric quadrupole interactions or internal magnetic hyperfine fields associated with electronic moments were important.

The contribution C_m is associated with Cu^{2+} magnetic moments that order at temperatures below 1K, depending on their concentration. In zero applied field C_m is not a simple Schottky anomaly. No doubt this reflects the existence of a distribution of effective magnetic fields associated with disorder in the spatial distribution of the moments and their interactions. Several different approximations to the high-temperature "tail" of the anomaly by expansions in inverse powers of temperature have been used, and they can be represented by the general expression $C_m = \Sigma A_{-n} T^{-n}$. In the presence of a magnetic field of a few T or more the anomaly is shifted to temperatures above 1K. It is the field dependence that suggests Cu^{2+} moments. If the concentration of moments is sufficiently low the anomaly may take the form of the Schottky anomaly expected for Cu^{2+} moments in the applied field (to within the accuracy of the data) but for higher concentrations, and depending on the field, the anomaly may still be broadened by the internal fields. The n_2 concententation of these moments is determined by the Schottky anomaly.

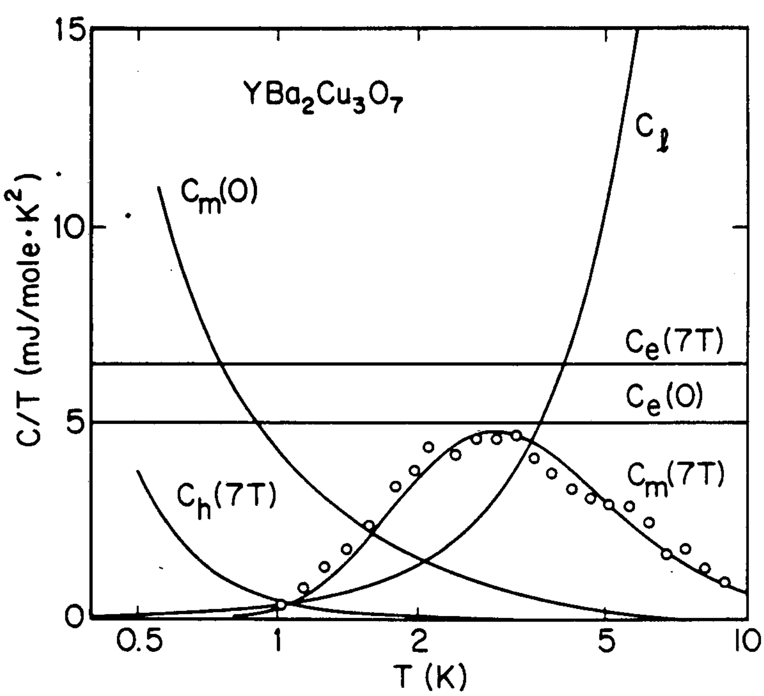


Figure 2. Components of the low-temperature specific heat for a YBCO sample.

The coefficient of the linear term is approximately linear in H, $\gamma(H)=\gamma(0)+(d\gamma/dH)H$. It is the H=0 component, $\gamma(0)$, that is unexpected, by comparison with the superconducting state specific heat of conventional superconductors. The H-proportional term is presumably of the same origin (5) as the analogous term in the mixed-state specific heat of conventional type-II superconductors – normal-state-like excitations in the vortex cores.

Figure 2 shows an analysis of low-temperature specific-heat data for YBCO into the four components for H=0 and 7T. The solid line through the points for $C_m(7T)$ is a Schottky function for Cu^{2+} moments with $n_2=0.0044$ moles Cu^{2+}/mole YBCO. The points were obtained by subtracting C_ℓ, C_h and C_e from C. The analysis was made by least-squares fits with the temperature dependences listed above.

ANALYSIS OF SPECIFIC HEAT NEAR T_c

Perhaps the most serious problem associated with specific-heat measurements on HTSC is the impossibility of quenching superconductivity (except very close to T_c) with the magnetic fields available in the laboratory. Thus, the relatively simple methods for separating the lattice and electronic contributions, and determining the zero-field specific-heat anomaly at T_c, which are so important for conventional superconductors, do not work for HTSC. The analysis of data near T_c is further complicated by the broadening of the anomaly by sample inhomogeneities.

In spite of these complications, most specific-heat data for HTSC can be consistently analyzed to obtain the mean-field component of the anomaly, $\Delta C(T_c)$. There are different methods of estimating $\Delta C(T_c)$ from the data, several of which are

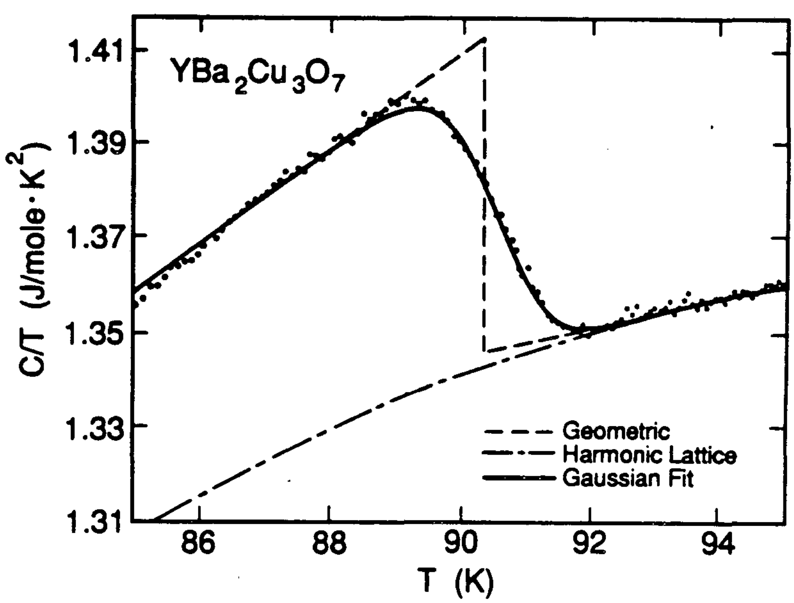


Figure 3. Specific-heat data for YBCO near T_c with several constructions used to determine $\Delta C(T_c)$ as described in the text.

illustrated in Fig. 3, with data obtained on a polycrystalline sample of YBCO. The dot-dash curve is an estimate of (C_ℓ + C_{en}) based on a harmonic lattice approximation (6) with the addition of a term proportional to temperature which is fitted to the data from 50 to 280K, with the region between 70 and 110K excluded from the fit, and the data below 70K corrected for a small contribution from C_{es} (n and s refer to normal and superconducting, respectively). The dashed lines in the figure represent simple linear extrapolations of the C/T data just above and just below T_c. T_c and $\Delta C(T_c)$ are determined by an entropy-conserving construction that equalizes the two areas between the dashed lines and the data. The height of the vertical dashed line, $\Delta C(T_c)/T_c$, is 66 mJ/mole.K^2 and T_c =90.3K. An entropy-conserving construction that uses the dot-dash curve corresponding to the harmonic-lattice background rather than the straight-line extrapolation above T_c gives $\Delta C(T_c)/T_c$ = 69 mJ/mole.K^2 and essentially the same value of T_c. The smooth curve through the data is the sum of the estimated lattice contribution and a term representing C_{es} calculated for a BCS superconductor with a Gaussian spread of T_c's. The fit was obtained by adjusting the value of γ for C_{es} and the width of the Gaussian distribution. The mean T_c is 91K, γ =45 mJ/mole.K^2 and $\Delta C(T_c)/T_c$=64 mJ/mole.K^2, in reasonable agreement with the other two estimates of $\Delta C(T_c)/T_c$. [γ is here used as a scaling factor to fit the observed specific-heat anomaly. Its high value relative to that determined for the normal state--16 mJ/mole.K^2 (7)-- is an indication of strong-coupling effects.]

The width of $\Delta C(T_c)$ in Fig.3 is probably largely due to sample inhomogeneities which tend to obscure the effects of fluctuations. Figure 4 shows an example of the specific heat for another YBCO sample which has been analyzed using only fluctuations to account for the width of the transition (8). [$\Delta C = C-(C_\ell + C_{en})$ was

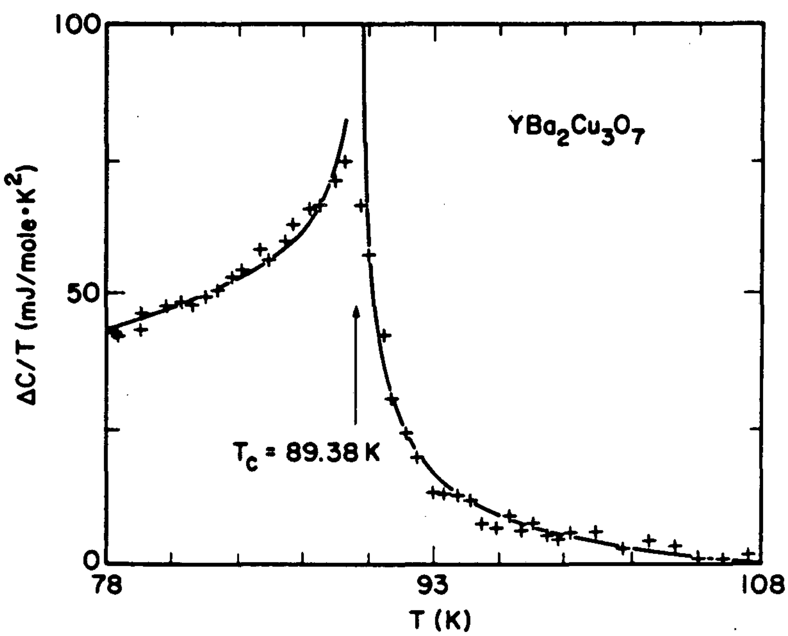


Figure 4. Specific heat of polycrystalline YBCO. The curves represent a fit by the expression for the fluctuation contribution given in the text.

obtained in a similar fashion to that described above for Fig. 3.] The continuous curves represent a BCS like C_{es} with T_c=89.38K; γ =41 mJ/mole.K^2 (γ is also used as a scaling factor here); and with an added 3-dimensional Gaussian fluctuation contribution (C_f) given by $C_f = A^{\pm}|T/T_c - 1|^{1/2}$. The values of A^+ ($T>T_c$) and A^- ($T<T_c$) are 0.51 and 0.24 J/mole.K, respectively.

VOLUME FRACTION OF SUPERCONDUCTIVITY

Independently of the sample-to-sample variation of the width of the anomaly, there is a strong sample dependence of $\Delta C(T_c)$. One obvious possibility is that the sample-to-sample variation of $\Delta C(T_c)$ corresponds to a sample-to-sample variation of f_s. This possibility can by tested by a comparison of values of $\Delta C(T_c)$ with the values of two other parameters derived from the specific-heat data that would also be expected to measure f_s, $d\gamma/dH$ and ΔS (defined below). If $d\gamma/dH$ corresponds to the mixed-state electronic specific heat, it should clearly be proportional to f_s. ΔS is defined in Fig. 5 (9). The shaded area represents the entropy decrease produced by the application of a magnetic field between the temperature at which the zero-field and in-field specific heat curves cross (T_x) and T_c. If the zero-field superconducting transition is incomplete, ΔS should also be proportional to f_s. The third law of thermodynamics requires that ΔS be equal to the area between the zero-field and in-field curves for $T<T_x$. The relation $\Delta S/T_x=\Delta\gamma$, where $\Delta\gamma$ is the value measured at low temperatures, has been found to hold to within a few percent for all samples for which it has been tested, suggesting that $d\gamma/dH$ is approximately constant over a wide

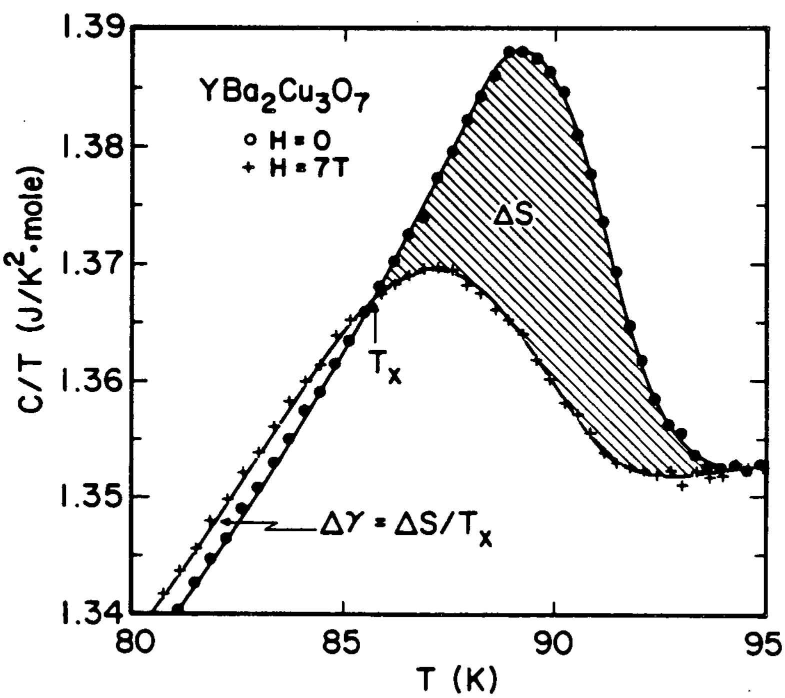


Figure 5. C/T versus T for H=0 and 7T. See text for a discussion of the relation between $\Delta\gamma$ and ΔS.

temperature range extending nearly to T_γ. However, it should be noted that although ΔS and $d\gamma/dH$ are not thermodynamically independent, empirically they are independent measures of f_s.

In fact, the three quantities $\Delta C(T_c)/T_c$, $d\gamma/dH$, and ΔS are mutually proportional, as illustrated in Fig. 6, where $d\gamma/dH$ and ΔS are plotted versus $\Delta C(T_c)/T_c$. [Since T_c is essentially constant for these samples, it does not matter whether $\Delta C(T_c)$ or $\Delta C(T_c)/T_c$ is used for this purpose.] The interpretation of all three quantities as measures of f_s is supported by these correlations. [It could be argued that the variations in $\Delta C(T_c)/T_c$, $d\gamma/dH$ and ΔS might be due to variations in the density of electron states. However, the temperature-independent term in the high-temperature susceptibility is constant, suggesting that the electron density of states is also constant.]

Although $\Delta C(T_c)/T_c$, $d\gamma/dH$ and ΔS are all proportional to f_s, there is at this point no means of identifying the values corresponding to $f_s=1$. For that purpose, the correlations of the three quantities with n_2 is useful, as shown in Fig. 7 for $\Delta C(T_c)/T_c$. The fact these parameters correlate with n_2 at all shows that a substantial number of the Cu^{2+} ions that contribute to n_2 must be located on the YBCO lattice. The scatter of the points in Fig. 7 probably reflects not only 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 $\Delta C(T_c)$.

The correlation between $\Delta C(T_c)/T_c$ and n_2 displayed in Fig. 7 implies a maximum value of $\Delta C(T_c)/T_c$ that is approximately 77 mJ/mole.K^2. For other values of $\Delta C(T_c)/T_c$, $f_s=[\Delta C(T_c)/T_c]/77$. Essentially the same conclusion has been reached by the Geneva group (10) on the basis of somewhat different, but related, evidence.

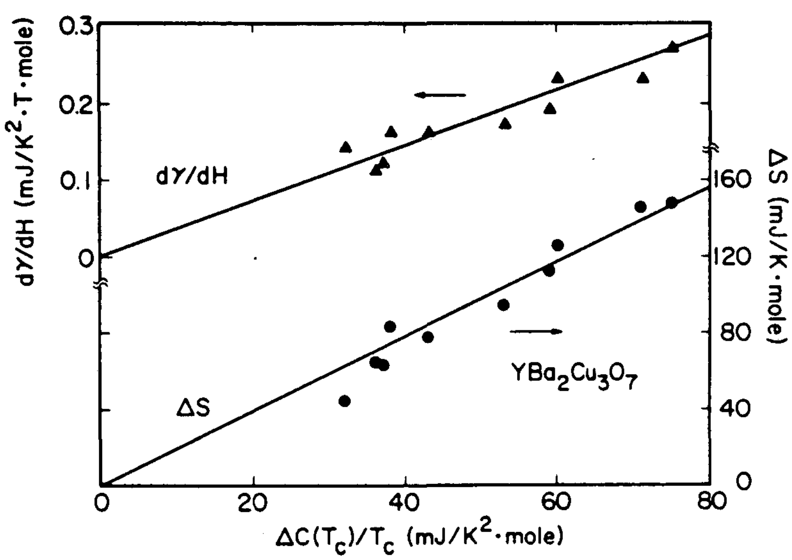


Figure 6. Correlation of $d\gamma/dH$ and ΔS with $\Delta C(T_c)/T_c$.

An interpretation of the above observations, consistent with the small values of ξ, is that defects suppress superconductivity in their immediate vicinity, leaving T_c unchanged elsewhere. The Cu^{2+} moments measured by n_2 may act as pair-breaking centers or they may constitute a measure of the concentration of another defect that has the primary role. Other evidence that supports this interpretation (but does not distinguish the two possibilities for the role of the Cu^{2+} moments) is the existence (7) of a contribution to $\gamma(0)$ that is proportional to n_2.

Another interesting correlation is that of the T=0 Debye temperature [$\theta(0)$], derived from B_3, with f_s. It is displayed in Fig. 8 and suggests that $\theta(0)$=545K for fully superconducting material and 345K for non-superconducting material. This correlation may be evidence in support of the conjecture that there is a change in the lattice accompanying the transition to the superconducting state, or it may simply be a direct effect of the defects on the vibration spectrum.

COUPLING STRENGTH AND ELECTRON DENSITY OF STATES

The value of f_s can be used in the analysis of specific-heat data near T_c to obtain information about the strength of the coupling. An example is illustrated in Fig. 9 with data for a YBCO sample prepared by the citrate pyrolysis method. The analysis is based on the α model (11), a model that takes into account the possibility of strong coupling effects. The thermodynamics of the transition corresponds to a gap with the BCS temperature dependence but scaled by a constant factor, represented by $\alpha \equiv \Delta_0/kT_c$. Application of the α model gives the value of α, determined by the shape of the anomaly, and also $f_s\gamma$, determined by the amplitude.

The dotted and solid curves in Fig. 9 represent, respectively, approximations to C_n and C_s. $C_n = C_\ell + \gamma T$, where C_ℓ is assumed to consist of dilatation and harmonic terms (6). C_n was obtained by fitting the data above 96K and between 62-65K, the region expected to include the temperature (T_x) at which $C_n = C_s$. The solid curve is

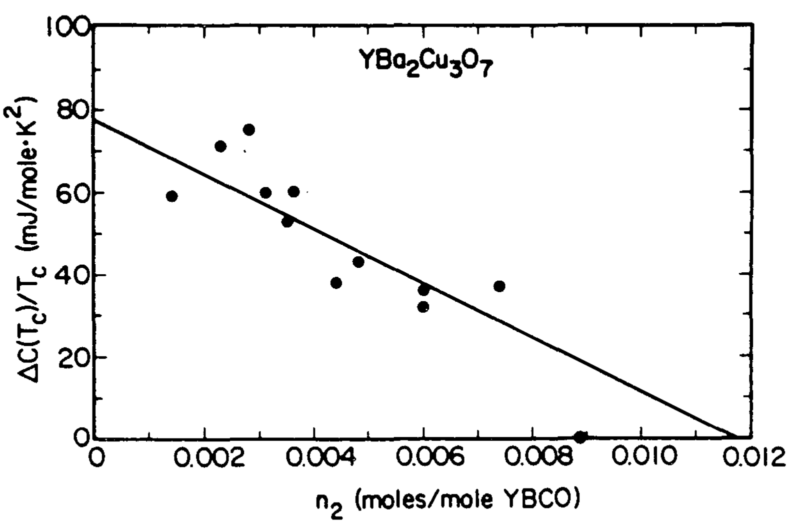


Figure 7. Correlation of $\Delta C(T_c)/T_c$ with n_2.

given by $C_s = C_\ell + f_s C_{es} + (1-f_s)\gamma T$, where C_{es} is calculated by assuming a Gaussian distribution of transition temperatures centered on $<T_c>$ with width ΔT_c. The fit parameters for C_s are given in Fig. 9. (The inclusion of a small fluctuation contribution would slightly improve the fit near 93K, but is not essential.) From the fit: $\gamma = 15 \pm 3$ mJ/mole.K^2 (for this sample $f_s = 0.83$); the gap ratio $2\Delta_0/kT_c = 6.8 \pm 0.6$, 1.9 times the weak-coupling BCS value; $\Delta C(T_c)/\gamma T_c = 5.3$, approximately three times the weak-coupling BCS value; $T_x/T_c = 0.69$ compared with 0.51 for the weak-coupling limit. These comparisons clearly point to the importance of strong-coupling effects.

The value of γ obtained by analysis of the specific-heat anomaly using the α model and the value of f_s is in reasonable agreement with values obtained by several other methods (4): 16 mJ/mole.K^2, from extrapolation of the n_2-proportional term in $\gamma(0)$ to the value of n_2 at which $f_s = 0$; 18 mJ/mole.K^2, from extrapolation of the H-proportional term in $\gamma(H)$ to $H_{c2}(0)$; and 20 mJ/mole.K^2 from an analysis of high-temperature specific-heat data. Comparison of these values with band-structure calculations which give the bare density of states $\gamma_{bs} = \gamma/(1+\lambda)$ provides an estimate of λ. The result, based on $\gamma = 17$ mJ/mole.K^2, and γ_{bs} = 16 mJ/mole.K^2 (12) to 13 mJ/mole.K^2 (13), is λ ~0.1-0.3. These relatively small values of λ are inconsistent with the strong-coupling effects deduced above if the coupling is via the phonons and the gap has the BCS temperature dependence.

ACKNOWLEDGEMENTS

This work was 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 No. DE-AC03-76SF00098.

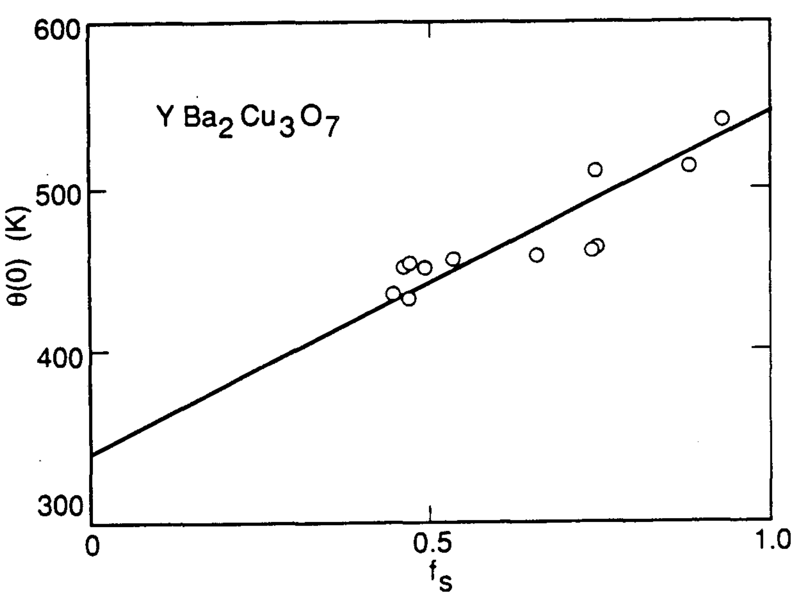


Figure 8. Low-temperature limiting Debye temperature as a function of f_s.

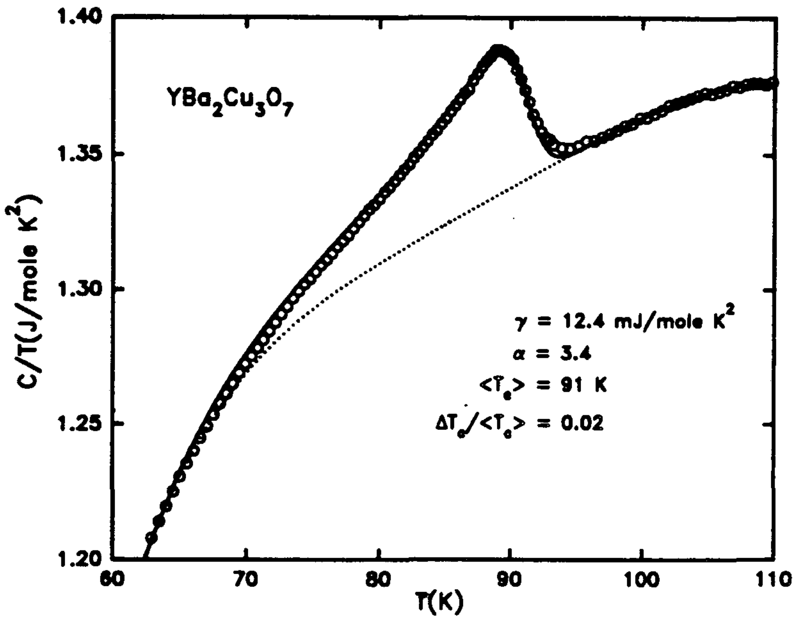


Figure 9. Fit of C to the α model. See text for discussion.

REFERENCES

1. N. E. Phillips et al., in: Novel Superconductivity, eds. S. A. Wolf and V. Z. Kresin (New York, NY: Plenum Press, 1987), 739.
2. The nonzero value of the zero-field "linear term", $\gamma(0)T$, had been observed in measurements at a number of laboratories early in 1987, and reported informally at several meetings (e.g., the 1987 APS March meeting). The first published reports were: M. E. Reeves et al., Phys. Rev. B35, 7207 (1987); L. E. Wenger et al., Phys. Rev. B35, 7213 (1987); B. D. Dunlap et al., Phys. Rev. B35, 7210 (1987).
3. P. W. Anderson et al., Phys. Rev. Lett. 58, 2790 (1987).
4. N. E. Phillips et al., in: Progress in Low-Temperature Physics 13, ed. D. E. Brewer (Amsterdam, The Netherlands: North-Holland, 1991), to be published.
5. K. Maki, Phys. Rev. A3, 702 (1965).
6. J. E. Gordon et al., Solid State Commun. 69, 625 (1989).
7. N. E. Phillips et al., Phys. Rev. Lett. 65, 357 (1990).
8. J. E. Gordon et al., Physica C 162-164, 484 (1989).
9. J. E. Gordon et al., Bull. Mater. Sci., to be published 1991.
10. A. Junod et al., Physica C 162-164, 1401 (1989).
11. H. Padamsee et al., J. Low Temp. Phys. 12, 387 (1973).
12. A. Massidda et al., Phys. Lett. A122, 198 (1987).
13. H. Krakauer et al., J. Superconductivity 1, 111 (1988).

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720