

SPECIFIC HEAT DATA OF HIGH- T_c SUPERCONDUCTORS: LATTICE AND ELECTRONIC CONTRIBUTIONS

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A high-temperature expansion for the harmonic portion of the lattice specific heat, of the form $C/3Nk = \sum_{n=0}^{\infty} B_n u^{-n}$, where $u = [(T/T_b)^2 + 1]$ and $T_b \approx 90$ K, is used to represent the lattice specific heats of the high- T_c superconductors $\text{DyBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ near and above T_c . With this expansion and published data it is possible to obtain values for the electronic specific heat coefficient (γ) of 38 ± 3 and 40 ± 5 mJ mol $^{-1}$ K $^{-2}$, respectively, for $\text{DyBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$. These values for γ , when combined with the observed $\Delta C(T_c)$ at T_c , are consistent with the BCS prediction that $\Delta C(T_c) = 1.43\gamma T_c$ for a superconductor in the weak-coupling limit, although the shape of the specific heat anomaly for the dysprosium compound gives evidence of a fluctuation contribution.

INTRODUCTION

THE BARDEEN-Cooper-Schrieffer (BCS) theory of superconductivity predicts that in the weak-coupling limit the jump in the specific heat at the transition temperature (T_c) is given by:

$$\Delta C(T_c) = 1.43\gamma T_c, \quad (1)$$

where γ is the coefficient in the specific heat of the normal electrons ($C_{en} = \gamma T$). For conventional superconductors it is relatively easy to measure both $\Delta C(T_c)$ and γ , and thus to determine whether or not BCS theory in the weak-coupling limit applies. However, in the case of the high temperature superconductors (HTSC), it is difficult to measure ΔC with assurance (see [1] for a discussion and an extensive set of references). More importantly, it is impossible to determine γ by the usual technique of measuring C in an applied magnetic field large enough to suppress the superconductivity, since the critical field for an HTSC is too large to be produced in the laboratory. Recent specific heat measurements have greatly improved the accuracy of the data near T_c . Nevertheless, a good test of equation (1) cannot be made without: (a) knowledge of the temperature dependence of the lattice specific heat near T_c and (b) a reasonably good estimate of the value of γ . In this note we shall indicate how it is

possible to analyze specific heat data (primarily) above T_c to obtain both (a) and (b).

A METHOD FOR APPROXIMATING THE LATTICE AND ELECTRONIC SPECIFIC HEAT ABOVE T_c

The specific heat of a system of $3N$ coupled harmonic oscillators is given by:

$$C_h = k \int_0^{E_{\max}} (E/kT)^2 e^{E/kT} (e^{E/kT} - 1)^{-2} g(E) dE, \quad (2)$$

where k is Boltzmann's constant, $g(E)$ is the density of states and $\int_0^{E_{\max}} g(E) dE = 3N$.

It was shown by Thirring [2] that for temperatures $T > E_{\max}/2\pi k$, C_h can be expanded in a series of the form:

$$C_h/3Nk = 1 + \sum_{n=1}^{\infty} D_n T^{-2n}, \quad (3)$$

where $D_n \propto \int_0^{E_{\max}} g(E) E^{2n} dE$. For example, in the case of a Debye solid, where $g(E) \propto E^2$, the expansion becomes:

$$\begin{aligned} C_h/3Nk = & 1 - \theta^2/20T^2 + \theta^4/560T^4 \\ & - \theta^6/18144T^6 + \theta^8/633600T^8 - \dots, \end{aligned} \quad (4)$$

where $\theta = E_{\max}/k =$ Debye temperature. However, it should be emphasized that equation (3) is valid (providing $T > E_{\max}/2\pi k$) not merely for the Debye

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solid, but for *any solid*, whatever the form of $g(E)$, so long as $g(E)$ is well-behaved and has a cut-off energy. Unfortunately, unless $T > E_{\max}/4k$, the series does not converge rapidly, as can be easily checked in the special case of equation (4). Sack, Maradudin and Weiss [3] pointed out, however, that it is possible to transform the series into one that converges considerably more rapidly than does the expansion in equation (3). One such transformation is:

$$C_h/3Nk = \sum_{n=0}^{\infty} B_n u^{-n} = 1 + \sum_{n=1}^{\infty} B_n u^{-n}, \quad (5)$$

where $u = [(T/T_b)^2 + 1]$ and $T_b \approx E_{\max}/2\pi k$. Sack *et al.* [3] show, for example, that in the case of the Debye solid at temperature $T = \theta/4$, equation (4) requires eight terms in the expansion to obtain a value for $C_h/3Nk$ which is correct to $\sim 0.2\%$, whereas equation (5) achieves an accuracy of $\sim 0.03\%$ with only four terms. The use of equation (5) thus permits the harmonic portion of the lattice heat capacity to be fitted reasonably well down to temperatures of ~ 50 K even if the effective Debye θ of the material is of the order of 500 K.

When fitting the heat capacity of an actual substance, it is, of course, important to recognize that the measured heat capacity will differ from the harmonic lattice contribution. In the case of an HTSC above T_c we can write $C_{\text{meas}} \approx C_h + C_x + AT$, where C_x is a possible contribution arising from crystal field effects and $A = \gamma + A_d + A_a$. Here γ is the normal electron specific heat coefficient, A_d is the dilatation correction ($C_p - C_v$) and A_a is any anharmonic contribution not included in A_d [4]. [The authors of [4] used this approach, with one term in the expansion in equation (3), to estimate high-temperature values of γ for AlS compounds.] For temperatures less than T_c , an analytic representation of the specific heat is more complicated. However, for the temperature region $T_c/3 < T < 2T_c/3$, the electronic specific heat (C_{es}) is relatively small, and can be approximated relatively simply (see below). In the following analysis we shall initially ignore the possible contribution of C_x . However, we shall return to this point at the end of the article, and will argue that where such a term is present, its contribution will have been properly accounted for by the analysis.

Figure 1 is a plot of the specific heat of $\text{DyBa}_2\text{Cu}_3\text{O}_7$ (DBCO). The data were taken from the graphs of Atake *et al.* [5]. The dashed curve is given by $C = C_D + \alpha T$, where $\alpha = 38 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and C_D is the specific heat of a Debye solid with $\theta = 547$ K, a value which was chosen to provide agreement with the data at 300 K. It is evident from the graph that the discrepancy between the data and the Debye specific

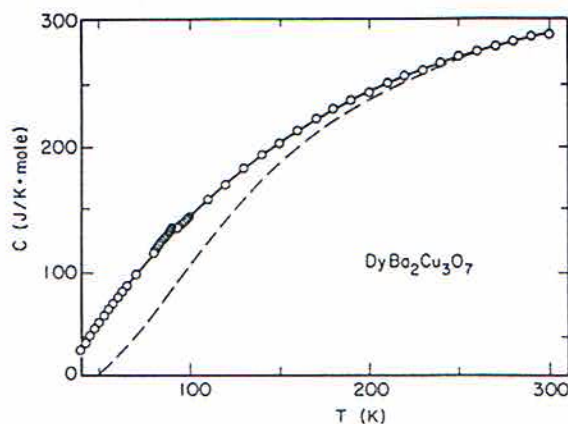


Fig. 1. C vs T for representative DBCO data taken from the figures in [5]. The dashed curve, chosen to fit the data at 300 K, is the sum of a Debye specific heat ($\theta = 547$ K) and a linear term. The solid curve is a fit to the data using equation (7) (see text for details).

heat increases with decreasing T , a result which can be summarized by saying that in the temperature domain shown, the "effective" θ for DBCO increases with increasing temperature (it can be easily checked that no single pair of θ and α values can bring the dashed curve into agreement with the data). The smooth curve which passes through all the experimental points in Fig. 1 except those near T_c was obtained by an iterative process in which a least-squares fit was first made to the data above 100 K and then to all data above 40 K save those in the vicinity of T_c . In the first step the data were fit with a polynomial of the form:

$$C_h/39R = (C_{\text{meas}} - AT)/39R = \sum_{n=0}^4 B_n u^{-n}, \quad (6)$$

where R is the gas constant, $u = [(T/T_b)^2 + 1]$ and $T_b = 87 \text{ K} \approx 547/2\pi$. A was varied until the least-squares fitting procedure yielded a value of 1.00 for B_0 . This procedure guarantees that the high temperature limit of C_h is $39R$, the DuLong-Petit value for a solid with 13 atoms per formula unit. The value of A which achieves this result for data above 100 K is $38 \pm 2 \text{ mJ mol}^{-1} \text{ K}^{-2}$. In the second step of the fitting procedure all the data above 40 K except those in the region 71 to 99 K were included in the least-squares fitting procedure. However, in making this fit, we replaced equation (6) by:

$$C_h/39R = \{C_{\text{meas}} - AT[1 + a(T - b)]/39R\} \\ = \sum_{n=0}^5 B_n u^{-n}, \quad (7)$$

where a and b are zero for the data above 100 K, and are adjustable constants for the data below 70 K. The term, $AT[1 + a(T - b)]$, is an approximation to C_{es} .

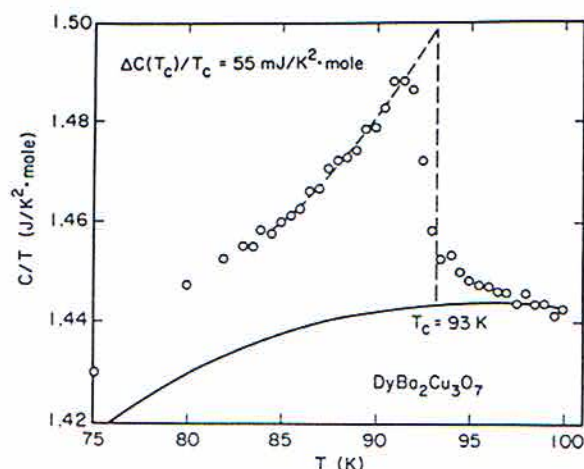


Fig. 2. C/T vs T in the vicinity of T_c for the DBCO data from [5]. The vertical dashed line is the entropy-conserving construction representing an ideal sharp normal-to-superconducting transition at T_c . The solid curve represents $(C_h + \gamma T)/T$ from the fit to the data above and below T_c using equation (7) (see text for details).

in this limited temperature interval. The fit was carried out with the constraint that $B_0 = 1.00$, and the constants a and b were varied until A had the same value ($38 \text{ mJ mol}^{-1} \text{ K}^{-2}$) as in step 1. It was found empirically that a and b were ~ 0.03 and $\sim 0.5 T_c$, values which are consistent with the BCS prediction that $C_{es} \approx \gamma T$ when $T \approx T_c/2$.

As noted, there are three contributions to the constant A . If A_d is assumed to be the same for DBCO as for $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO), then the use of the isothermal compressibility and bulk modulus data of Lang *et al.* [6], gives $A_d \sim 1 \text{ mJ mol}^{-1} \text{ K}^{-2}$. The value of A_s is not known, but if the results on the Al5 compounds are any guide [4], then A_s can be either positive or negative and have a magnitude of $\sim 1 \text{ mJ mol}^{-1} \text{ K}^{-2}$. With such estimates for A_s and A_d it is reasonable to write $\gamma \approx 38 \pm 3 \text{ mJ mol}^{-1} \text{ K}^{-2}$, where the uncertainty in γ reflects both uncertainties in the fitting procedure and an expectation that A_s has a magnitude that does not exceed $\sim 1 \text{ mJ mol}^{-1} \text{ K}^{-2}$.

If the assumptions which underlie the above fitting procedure are valid, then this method allows an estimate of C_{es} as well as of C_{en} and the lattice specific heat. Figure 2 is a graph of $(C_{\text{meas}})/T$ and of $(C_h + \gamma T)/T$ vs T in the vicinity of T_c , where the values of C_{meas} are taken from Fig. 3 of [5]. The difference between the curve and the experimental points below T_c is $\sim (C_{es} - \gamma T)/T$. At T_c this difference is just $\Delta C(T_c)/T_c = [C_{es}(T_c) - C_{en}(T_c)]/T_c$. The dashed line in Fig. 2 is an entropy-conserving construction which indicates that T_c is $\sim 93 \text{ K}$. The $\Delta C(T_c)/T_c$ asso-

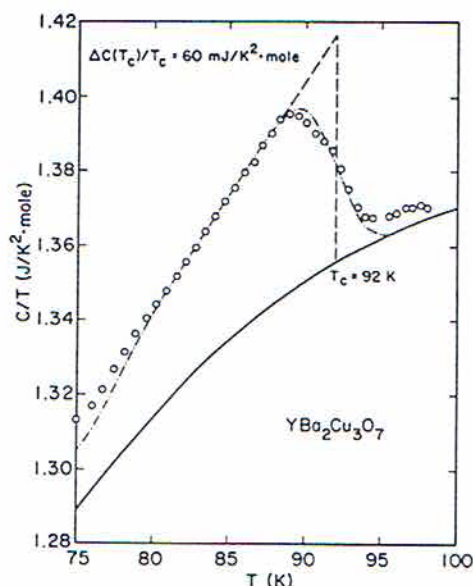


Fig. 3. C/T vs T in the vicinity of T_c for the YBCO data from [10]. The vertical dashed line has the same meaning as in Fig. 2. The solid curve represents $(C_h + \gamma T)/T$ from a fit to the data of [9] above and below T_c using equation (7) (see text for details), while the dashed-dotted line represents the electronic specific heat of a BCS superconductor with a Gaussian distribution of T_c 's.

ciated with the dashed line is $\sim 55 \text{ mJ mol}^{-1} \text{ K}^{-2}$, a value which, when combined with $\gamma = 38 \text{ mJ mol}^{-1} \text{ K}^{-2}$, yields $\Delta C(T_c)/\gamma T_c \approx 1.45$, in good agreement with equation (1). Nonetheless, the appearance of the specific heat anomaly is different from that for a conventional BCS superconductor. As is evident, the data exhibit an excess specific heat "tail" above T_c . They also drop more sharply below T_c than would be expected for a mean-field BCS transition. Both characteristics are typical of a fluctuation contribution to the specific heat, as has been pointed out by Inderhees *et al.* [7].

A similar analysis was done for YBCO using the data of Laegreid *et al.* [8] and of Boerio-Goates and co-workers [9]. In these analyses the data in the region of T_c were omitted, as were those near the anomaly at 210 K in the results of Laegreid *et al.* [8]. For the data of [8], we obtain $\gamma = 44 \pm 5 \text{ mJ mol}^{-1} \text{ K}^{-2}$, and for those of [9] $\gamma = 40 \pm 4 \text{ mJ mol}^{-1} \text{ K}^{-2}$. We have also used the fit obtained with the data from [9] to analyze the YBCO data of Fisher *et al.* [10] near T_c . In Fig. 3 we plot C_{meas}/T as well as the predicted variation of $(C_h + \gamma T)/T$. The data of [10] were taken only to 98 K , but they appear to be approaching the curve obtained from the data of [9]. The entropy-conserving construction yields $\Delta C(T_c)/\gamma T_c \approx 1.5$. The dashed-dotted line through the data corresponds to the electronic specific

Table 1. Fit parameters

Constant	DBCO	YBCO
A (mJ mol $^{-1}$ K $^{-2}$)	38.4	40.4
T_b (K)	87.1	92.3
a (K $^{-1}$)	0.03	0.03
b (K)	60	50
B_0	1.0000	1.0000
B_1	-2.1697	-2.1275
B_2	3.4681	3.3919
B_3	-5.1329	-4.4418
B_4	4.8203	2.4272
B_5	-2.0999	-0.11041

heat of a weakly-coupled BCS superconductor which has a Gaussian distribution of T_c 's [11] with a mean $T_c = 92$ K, a half width $\delta T_c = 1.5$ K and a $\gamma = 39$ mJ mol $^{-1}$ K $^{-2}$.

In Table 1 we list the values for A , T_b , a , b and B_n ($n = 0$ to 5) for DBCO [5] and YBCO [9]. With these values, almost all the data (except, of course, the points in the vicinity of T_c) can be fit to 0.3% or better within the range of the fit. However, because the B_n oscillate in sign and are of comparable magnitude, they cannot be used to extrapolate beyond the fitting region.

It should be emphasized that the fitting procedure we have used yields a value for A by assuming the expansion coefficient B_0 to be exactly one. If data contain systematic errors of the order of 1% or more, the value of A (and therefore of γ) is seriously affected. Furthermore, the value of A depends upon the assumption made concerning the number of atoms per formula unit. In our analysis we have assumed 7 oxygens. If a (perhaps more reasonable) value of 6.9 oxygens/f.u. is used, γ is increased by 4–5 mJ mol $^{-1}$ K $^{-2}$.

It would appear that in our analysis we have not taken into account a possible contribution (C_c) to the measured specific heat from crystal-field splittings of the ground state of the rare earth ion. In the case of YBCO no such term is present because the yttrium ion has a non-degenerate ground state. However, in the case of DBCO the $J = 15/2$ ground state of Dy is split into Kramer's doublets by the crystal field. The splittings have very recently been measured by Furrer *et al.* [12], and it is therefore possible to calculate C_c . The calculated C_c has a maximum at ~ 20 K, which is in agreement with the measurements of Dunlap *et al.* [13], and then decreases with increasing T . At 100 K C_c is $\sim 2.5\%$ of C_{meas} and at 300 K it is $\sim 0.8\%$. The effect of C_c on the data analysis has been tested by subtracting the calculated values from the data above 100 K and

then using equation (6) and the procedures described above to obtain values for A and the B_n . It was found that the value of A is reduced from 38 to 37 mJ mol $^{-1}$ K $^{-2}$ and the values of the B_n are altered slightly. This change in A lies within the uncertainties already discussed. It is not surprising that equations (6) and (7) can be used to represent the specific heat of DBCO as well as that of YBCO, even though the former contains a contribution from crystal field effects. For temperatures above 40 K the temperature dependence of C_v , like that of C_h , is well-represented by the approximations used in our analysis. In particular, the high-temperature "tail" of C_v can be well fitted to a power series of the form $\sum_{n=1}^4 B'_n u_n^{-1}$. Thus, the principal effect of C_c is to alter somewhat the values which the B_n would have were the crystal field not present, rather than to influence the value of γ inferred from the analysis. Therefore, in equations (6) and (7), C_h may be thought of as including the crystal field as well as harmonic lattice contributions to the measured specific heat.

We have also examined the YBCO data of Lang *et al.* [6]. These data, like those of Junod *et al.* [14], are considerably lower than those in [8] and [9]. While the data in [6] can be fit using the procedures described above, they yield a large negative value for A , a result which would imply that the dominant contribution to the linear term comes from A_c . Finally, it should be mentioned that the above analysis makes no assumption about the $\gamma(0)T$ term present in the low temperature specific heat of YBCO and other high T_c superconductors [1]. This term, if it persists to higher temperatures, would simply affect the values of the constants A , a and b in equation (7).

SUMMARY

By fitting accurate specific heat data on the HTSC over the temperature range ~ 40 to 300 K, it is possible to decompose the measured specific heat into lattice and electronic contributions with a reasonable degree of confidence. In the case of YBCO and DBCO we find that γ is 40 ± 5 mJ mol $^{-1}$ K $^{-2}$ and 38 ± 3 mJ mol $^{-1}$ K $^{-2}$, respectively. These values are consistent with the weak-coupling BCS prediction that $\Delta C(T_c)/\gamma T_c = 1.43$. It is, perhaps, surprising that γ values as large as these persist to temperatures as high as 300 K. It is possible that the method of data analysis reveals only the leading, constant, part of a temperature-dependent γ . Certainly, very accurate specific heat measurements made at higher temperatures could shed light on this matter, and thereby test the recent predictions of Kresin *et al.* [15].

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REFERENCES

1. R.A. Fisher, J.E. Gordon & N.E. Phillips, to be published in the October 1988 issue of *J. Superconductivity*.
2. H. Thirring, *Physik Z.* **14**, 867 (1913); **15**, 127, 180 (1914).
3. R.A. Sack, A.A. Maradudin & G.H. Weiss, *Phys. Rev.* **124**, 717 (1961).
4. G.S. Knapp, S.D. Bader & Z. Fisk, *Phys. Rev.* **B13**, 3783 (1976).
5. T. Atake, Y. Takagi, T. Nakamura & Y. Saito, *Phys. Rev.* **B37**, 552 (1988).
6. M. Lang, T. Lachner, S. Riegel, F. Steglich, G. Weber, T.J. Kim, B. Luthi, B. Wolf, H. Rietschel & M. Wilhelm, *Z. Phys.* **B69**, 459 (1988).
7. S.E. Inderhees, M.B. Salamon, N. Goldenfield, J.P. Price, B.G. Pazol, D.M. Ginsberg, J.Z. Liu & G.W. Crabtree, *Phys. Rev. Lett.* **60**, 1178 (1988).
8. T. Laegreid, K. Fossheim, O. Traettaberg, E. Sandvold & S. Julsrud, *Physica* **C153-155**, 1026 (1988).
9. J. Boerio-Goates, private communication.
10. R.A. Fisher, J.E. Gordon, S. Kim, N.E. Phillips & A.M. Stacy, *Physica* **C153-155**, 1092 (1988).
11. S.D. Bader, N.E. Phillips & E.S. Fisher, *Phys. Rev.* **B12**, 4929 (1975).
12. A. Furrer, P. Allenspach & F. Hulliger, *Proceedings of the 6th International Conference on Crystal-Field Effects and Heavy Fermions*, Frankfurt, FRG, July 18-21, 1988; and to be published in *J. Magn. Magn. Mater.*
13. B.D. Dunlap, M. Slaski, D.G. Hinks, L. Soderholm, M. Beno, K. Zhang, C. Segre, G.W. Crabtree, W.K. Kwok, S.K. Malik, I.K. Schuller, J.D. Jorgensen & Z. Sungaila, *J. Magn. Magn. Mater.* **68**, L139 (1987).
14. A. Junod, A. Bezing, D. Cattani, M. Decroux, D. Eckert, M. Francois, A. Hewat, J. Muller & K. Yvon, *Helv. Phys. Acta* **61**, 460 (1988).
15. V.Z. Kresin, G. Deutscher & S.A. Wolf, unpublished.