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SPECIFIC HEAT DATA OF HIGH-\(T_c\) SUPERCONDUCTORS:

LATTICE AND ELECTRONIC CONTRIBUTIONS


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ABSTRACT

A high-temperature expansion for the harmonic portion of the lattice specific heat, of the form \(C/3Nk = 1 + \sum_{n=0}^{\infty} B_n u^{-n}\), where \(u=[(T/T_b)^2+1]\), is used to represent the lattice specific heats of the high-\(T_c\) superconductors Dy\(\text{Ba}_2\text{Cu}_3\text{O}_7\) and Y\(\text{Ba}_2\text{Cu}_3\text{O}_7\) near and above \(T_c\). With this expansion and published data it is possible to obtain values for the electronic specific heat coefficient \((\gamma)\) of 38\(\pm\)3 and 40\(\pm\)5 mJ/mole K\(^2\), respectively, for Dy\(\text{Ba}_2\text{Cu}_3\text{O}_7\) and Y\(\text{Ba}_2\text{Cu}_3\text{O}_7\). These values for \(\gamma\), 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 give 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:

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

where $\gamma$ 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 $\gamma$, 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 $\Delta C$ with assurance (see Ref. 1 for a discussion and an extensive set of references). More importantly, it is impossible to determine $\gamma$ 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 Eq. (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 $\gamma$. 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:

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

where $k$ is Boltzmann's constant, $g(E)$ is the density of states and $\int g(E) dE = 3N$.

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

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

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

$$\frac{C_h}{3Nk} = 1 - \theta^2/20T^2 + \theta^4/560T^4 - \theta^6/18144T^6 + \theta^8/633600T^8 - \ldots,$$  \hspace{1cm} (4)

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

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

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

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
\[
C_{\text{meas}} = C_h + AT, \quad \text{where} \quad A = \gamma + A_d + A_a.
\]
Here \( \gamma \) is the normal electron specific heat coefficient, \( A_d \) is the dilatation correction \((C_P-C_V)\) and \( A_a \) is an anharmonic term which arises because the normal mode frequencies of the lattice may be temperature-dependent. [The authors of Ref. 4 used this approach, with one term in the expansion term in Eq. (3), to estimate high-temperature values of \( \gamma \) for Al5 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).

Figure 1 is a plot of the specific heat of DyBa\(_2\)Cu\(_3\)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, \quad \text{where} \quad \alpha = 38 \text{ mJ/mole K}^2 \quad \text{and} \quad C_D \quad \text{is the specific heat of a Debye solid with} \quad \theta = 547K, \quad \text{a value which was chosen to provide agreement with the data at} \quad 300K. \quad \text{It is evident from the graph that the discrepancy between the data and the Debye specific heat increases with decreasing} \quad T, \quad \text{a result which can be summarized by saying that in the temperature domain shown, the "effective"} \quad \theta
for DBCO increases with increasing temperature (it can be easily checked that no single pair of $\theta$ and $\alpha$ 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 100K and then to all data above 40K save those in the vicinity of $T_c$. In the first step the data were fit with a polynomial of the form:

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

where $R$ is the gas constant, $u = [(T/T_b)^2+1]$ and $T_b = 87K = 547/2\pi$. $A$ 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 100K is $38\pm2$ mJ/mole K$^2$. In the second step of the fitting procedure all the data above 40K except those in the region 71 to 99K were included in the least-squares fitting procedure. However, in making this fit, we replaced Eq. (6) by:

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

where $a$ and $b$ are zero for the data above 100 K, and are adjustable constants for the data below 70K, and that term is an adequate approximation to $C_{es}$ 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 ($38$ mJ/mole K$^2$) as in step 1. It was found empirically that $a$ and $b$ were $-0.03$ and $-0.5T_c$, values which are consistent with the BCS prediction that $C_{es} = \gamma T$ when $T = T_c/2$. 
As noted, there are three contributions to the constant $A$. If $A_d$ is assumed to be the same for DBCO as for $YBa_2Cu_3O_7$ (YBCO), then the use of the isothermal compressibility and bulk modulus data of Lang et al.,\textsuperscript{6} gives $A_d = -1$ mJ/mole K$^2$. The value of $A_a$ is not known, but if the results on the Al5 compounds are any guide\textsuperscript{4}, then $A_a$ can be either positive or negative and have a magnitude of $\sim 1$ mJ/mole K$^2$. With such estimates for $A_a$ and $A_d$ it is reasonable to write $\gamma = 38 \pm 3$ mJ/mole K$^2$, where the uncertainty in $\gamma$ reflects both uncertainties in the fitting procedure and an expectation that $A_a$ has a magnitude that does not exceed $-1$ mJ/mole 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 $(C_{es}/T)$ and of $(C_{en} + \gamma T)/T$ versus $T$ in the vicinity of $T_c$, where the values of $C_{es}$ are taken from Fig. 3 of Ref. 5. The difference between the curve and the experimental points below $T_c$ is $(C_{es} - \gamma T)/T$. 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 $\sim 92$K. The $\Delta C(T_c)/T_c$ associated with the dashed line is $-55$ mJ/mole K$^2$, a value which, when combined with $\gamma = 38$ mJ/mole K$^2$, yields $\Delta C(T_c)/\gamma T_c = 1.45$, in good agreement with Eq. (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 be Inderhees et al.\textsuperscript{7}

A similar analysis was done for YBCO using the data of Laegreid et al.\textsuperscript{8}
and of Boerio-Goates and coworkers. In these analyses the data in the
region of $T_c$ were omitted, as were those near the anomaly at 210K in the
results of Laegreid et al. For the data of Ref. 8, we obtain $\gamma = 44 \pm 5$ mJ/mole
K$^2$, and for those of Ref. 9 $\gamma = 40 \pm 4$ mJ/mole K$^2$. We have also used the fit
obtained with the data from Ref. 9 to analyze the YBCO data of Fisher et al. near $T_c$. In Fig. 3 we plot $C_{\text{meas}} / T$ as well as the predicted variation of
$(C_{\text{h}} + \gamma T) / T$. The data of Ref. 10 were taken only to 98K, but they appear to be
approaching the curve obtained from the data of Ref. 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 heat of a weakly-coupled BCS
superconductor which has a Gaussian distribution of $T_c$'s with a mean $T_c = 92K$, a
half width $\delta T_c = 1.5K$ and a $\gamma = 39$ mJ/mole K$^2$.

In Table I we list the values for $A$, $T_b$, $a$, $b$ and $B_n$ (n=0 to 5) for DBCO
(Ref. 5) and YBCO (Ref. 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 $\gamma$) 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, $\gamma$ is increased by 4-5 mJ/mole K$^2$.

We have also examined the YBCO data of Lang et al. These data, like those
of Junod et al.\textsuperscript{12}, are considerably lower than those in Refs. 8 and 9. While the data in Ref. 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 $A_a$. 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.\textsuperscript{1} This term, if it persists to higher temperatures, would simply affect the values of the constants $A$, $a$ and $b$ in Eq. (7).

**Summary**

By fitting accurate specific heat data on the HTSC over the temperature range -40 to 300K, 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 $\gamma$ is $40\pm5$ mJ/mole K\textsuperscript{2} and $38\pm3$ mJ/mole K\textsuperscript{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 $\gamma$ values as large as these persist to temperatures as high as 300K. It is possible that the method of data analysis reveals only the leading, constant, part of a temperature-dependent $\gamma$. 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.\textsuperscript{13}
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REFERENCES


2. H. Thirring, Physik Z. 14, 867 (1913); 15, 127, 180 (1914).


### TABLE I - FIT PARAMETERS

<table>
<thead>
<tr>
<th>Constant</th>
<th>DBCO</th>
<th>YBCO</th>
</tr>
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<tr>
<td>$A$ (mJ/mole K$^2$)</td>
<td>38.4</td>
<td>40.4</td>
</tr>
<tr>
<td>$T_b$ (K)</td>
<td>87.1</td>
<td>92.3</td>
</tr>
<tr>
<td>$a$ (K$^{-1}$)</td>
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<td>0.03</td>
</tr>
<tr>
<td>$b$ (K)</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td>$B_0$</td>
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<td>3.3919</td>
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<td>-4.4418</td>
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<tr>
<td>$B_4$</td>
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<td>$B_5$</td>
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<td>-0.11041</td>
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FIGURE CAPTIONS

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

Fig. 2. C/T vs T in the vicinity of Tc for the DBCO data from Ref. 5. The vertical dashed line is the entropy-conserving construction representing an ideal sharp normal-to-superconducting transition at Tc. The solid curve represents (Cn+γT)/T from the fit to the data above and below Tc using Eq. (7) (see text for details).

Fig. 3. C/T vs T in the vicinity of Tc for the YBCO data from Ref. 10. The vertical dashed line has the same meaning as in Fig. 2. The solid curve represents (Cn+γT)/T from a fit to the data of Ref. 9 above and below Tc using Eq. (7) (see text for details), while the dashed-dotted line represents the electronic specific heat of a BCS superconductor with a Gaussian distribution of Tc's.
Fig. 1

DyBa$_2$Cu$_3$O$_7$

C (J/K·mole)

T (K)
\[ \Delta C(T_c)/T_c = 55 \text{ mJ/K}^2 \text{ mole} \]

\[ T_c = 93 \text{ K} \]

\[ \text{DyBa}_2\text{Cu}_3\text{O}_7 \]
$\Delta C(T_c)/T_c = 60 \text{ mJ/K}^2\text{ mole}$

$T_c = 92 \text{ K}$

$\text{YBa}_2\text{Cu}_3\text{O}_7$