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SPECIFIC HEAT OF $\text{YBa}_2\text{Cu}_3\text{O}_7$

by

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Specific Heat of YBa$_2$Cu$_3$O$_7$


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Specific heat measurements, including measurements in magnetic fields and at both low temperatures and near $T_c$, on a number of YBa$_2$Cu$_3$O$_7$ samples have revealed several correlations among strongly sample dependent parameters. These correlations suggest that the sample dependence of the parameters reflects a sample dependence of the volume fraction of superconductivity, which is in turn correlated with a low concentration of Cu$^{2+}$ moments. The correlations give a criterion for recognizing the values of the parameters characteristic of the fully superconducting material. Preliminary results on the effects of sample heat treatment are reported. New data on the "linear term" is presented and discussed.

1. INTRODUCTION

The sample-to-sample variation in the properties of high-$T_c$ materials is a general and serious problem in connection with attempts to recognize intrinsic properties and distinguish them from effects associated with impurity phases or other defects. The specific heat (C) is unique among commonly measured properties in giving a true volume average of bulk properties, and therefore can play a special role in understanding the sample dependence [1]. Measurements at LBL on a variety of YBa$_2$Cu$_3$O$_7$ (YBCO) samples, including a number made in other laboratories, have revealed correlations between a number of sample-dependent parameters that suggest that the volume fraction of superconductivity ($f_s$) is strongly sample dependent (and therefore probably a major factor in the variation of properties in general) and that the non-superconducting regions are associated with a low
concentration \((n_2)\) of \(\text{Cu}^{2+}\) magnetic moments \([2,3]\). In addition to measurements on a large number of samples, recognition of these correlations required a unique combination of measurements in magnetic fields \((H)\) and at both low temperatures and near \(T_c\) -- all made on the same samples.

2. SPECIFIC HEAT-DERIVED PARAMETERS RELEVANT TO THE VOLUME FRACTION OF SUPERCONDUCTIVITY

Two of the parameters derived from \(C\) that are relevant to the determination of \(f_s\) are defined in Fig. 1: \(\Delta C(T_c)/T_c\), here defined by a simple entropy-conserving construction, is a measure of the magnitude of the specific heat anomaly at \(T_c\); \(\Delta S\) is a measure of the effect of a magnetic field of \(7T\) on that anomaly. These are both parameters that might be expected to be proportional to \(f_s\). The other parameters of interest in this connection are derived by an analysis of the low-temperature \(C\) into its components: the lattice contribution \((C_L)\); the "linear term" \((C_c)\); a contribution associated with \(\text{Cu}^{2+}\) magnetic moments \((C_m)\); and a hyperfine contribution \((C_h)\) that occurs only for \(H\neq 0\). The analysis of \(C\) into these four components is illustrated for a typical YBCO sample in Fig. 2. The linear term has a field dependence that can be represented by

\[
C_c(H)/T = \gamma^*(H) = \gamma^*(0) + (d\gamma^*/dH)H,
\]

where the \(H\)-proportional term corresponds to the mixed-state electron specific heat that is well known in conventional type II superconductors and its coefficient, \(d\gamma^*/dH\), should also be proportional to \(f_s\). For \(H=0\) the contribution of the \(\text{Cu}^{2+}\) moments appears as the high-temperature tail of a broadened Schottky-like anomaly produced by the distribution of internal fields; for an applied field \(H=7T\), which is large compared with the internal fields,
it is well approximated by the Schottky anomaly labeled $C_m(7T)$ in Fig. 2. The quality of the fit to the 7T data is indicated by comparison of the experimental points, from which the other contributions have been subtracted, with the Schottky curve. The amplitude of the Schottky curve determines $n_2$.

Thus, the measured parameters include three that should be proportional to $f_s$, and in principle any one of them could be used to calculate $f_s$ if the value for a fully superconducting, $f_s=1$, sample were known:

$$\frac{d\gamma^*/dH}{[d\gamma^*/dH]_{f_s=1}} = \frac{\Delta C(T_c)}{[\Delta C(T_c)]_{f_s=1}} = \frac{\Delta S}{[\Delta S]_{f_s=1}} = f_s. \tag{2}$$

Since none of the denominators in Eq. 2 is known, a least-squares procedure that gave equal weight to each of the parameters was used to derive the most consistent relative values of $f_s$. The results are shown in Fig. 3, where the values of the three parameters define a single value of $f_s$ for each sample, and each parameter has been scaled by a factor (the same for all samples) chosen to minimize the deviations from a common line through the origin. In addition to giving relative values of $f_s$, this construction demonstrates the mutual proportionality of $d\gamma^*/dH, \Delta C(T_c)/T_c$ and $\Delta S$, and therefore supports the suggestion that each is a measure of $f_s$.

There is also a correlation of $f_s$ with $n_2$, shown in Fig. 4, that provides the basis for putting $f_s$ on an absolute basis. It shows that $f_s$ decreases with increasing $n_2$, suggesting that the Cu$^{2+}$ moments are in some way associated with a defect that suppresses the transition to the superconducting state, and that extrapolation back to $n_2=0$ should identify the point on the $f_s$ axis at which the absolute value of $f_s$ is $f_s=1$ (see Fig. 4). With this identification
the values of $d\gamma^*/dH$, $\Delta C(T_c)/T_c$, $\Delta S$ and all other specific-heat derived parameters, for a fully superconducting sample, are determined. The correlation of $n_2$ with $f_s$, i.e., with the superconductivity-related parameters $d\gamma^*/dH$, $\Delta C(T_c)/T_c$ and $\Delta S$, shows that these Cu$^{2+}$ moments must be located, at least in substantial measure, on the YBCO lattice. However, that correlation (Fig. 4) is clearly less precise than those among $d\gamma^*/dH$, $\Delta C(T_c)/T_c$ and $\Delta S$ themselves (Fig. 3) suggesting that, as expected, some of these moments are in impurity phases.

3. SOME EFFECTS OF HEAT TREATMENT ON THE VOLUME FRACTION OF SUPERCONDUCTIVITY

The interpretation of the sample-to-sample variation of the properties of YBCO as reflecting a corresponding variation of $f_s$ raises an obvious question: How is $f_s$ affected by sample preparation techniques? As part of an effort to answer this question, a ceramic sample of YBCO has been subjected to a series of heat treatments—two successive quenches into liquid nitrogen after heating to 200°C (comparable quenches have occasionally been used to fix the oxygen stoichiometry); a rapid cooling through the tetragonal/orthorhombic (T/O) transition (actually from 950°C to 350°C); and finally, "reconstitution" by annealing at 950°C and slow cooling to 350°C—with intermediate measurements of $f_s$, $n_2$, and resistivity ($\rho$). Since the superconducting properties are also sensitive to oxygen content, the oxygen stoichiometry was monitored by high temperature susceptibility measurements which showed that no significant changes occurred. Table I gives the value of $f_s$ determined by $\Delta C(T_c)$, $n_2$ and, for comparison, $f_s(n_2)$, the value of $f_s$ derived from $n_2$ and its relation to $f_s$ shown in Fig. 4.
The first quench reduced $f_s$ from 0.85 to 0.78; increased $n_2$, but by a larger relative amount; and changed $\rho$ dramatically, increasing its magnitude and altering the T-proportional behavior (see Fig. 5). (Changes in $\rho$ of this kind have been attributed to changes in oxygen content, but evidently they can be produced by the quench itself when a quench is used to fix the oxygen stoichiometry.) The second quench, and the rapid cooling through the T/O transition produced further reductions in $f_s$ but no significant increases in $n_2$. The second quench caused a small further increase in $\rho$; reheating to 950°C, even with rapid cooling through the T/O transition, restored $\rho$ to its original value. Apparently the defects that changed $\rho$, that were produced in the first quench, were completely repaired by heating to 950°C. Finally, after reconstitution at 950°C and slow cooling to 350°C, $f_s$ increased and $n_2$ decreased, but the volume fraction of superconductivity remained lower than in the original sample [4].

4. THE LINEAR TERM

There has been a great deal of interest in the zero-field contribution to the linear term, $\gamma^*(0)$ in Eq. (2), because it has no counterpart in conventional superconductors. In early measurements [5] it was shown that impurity phases, particularly BaCuO$_2$, could make significant contributions to $\gamma^*(0)$, but it was often concluded that there was an "intrinsic" contribution as well. It has also been suggested [2] that $\gamma^*(0)$ could be accounted for by a sum of two contributions produced by, respectively, the impurity phases and the normal regions associated with the Cu$^{2+}$ moments present in concentration $n_2$. That suggestion was based on using the concentration of Cu$^{2+}$ moments in impurity phases ($n_1$) as a measure of the contribution of those phases to $\gamma^*(0)$. The moments that order below 1K in zero
applied field, affect the superconducting properties (see Fig. 4), and contribute to the
Schottky anomaly in Fig. 2, are present in concentration $n_2$; most of those that are present
in impurity phases, in concentration $n_1$, order at higher temperatures and do not contribute
to the Schottky anomaly. Both kinds contribute to the Curie-Weiss term in the high
temperature susceptibility, which therefore determines the total concentration, $n = n_1 + n_2$.
Since $n_2$ is determined by the low-temperature in-field $C$, both $n_1$ and $n_2$ are known. An
analysis of $\gamma^*(0)$ based on the relation of $\gamma^*(0) = \gamma_0 + \gamma_1 n_1 + \gamma_2 n_2$, where $\gamma_0$ is an intrinsic contribution, led to the conclusion that $\gamma_0$ was less than $1mJ/K^2.mole$, and negligible to
within the accuracy of the data. The conclusion was that the data could be explained
without invoking an intrinsic contribution. The figure showing the $n_1$- and $n_2$-proportional
ccontributions is reproduced here as Fig. 6.

In connection with the interpretation of the linear term in YBCO, it is noteworthy that,
in spite of continued attention to sample quality, it seems that no sample has shown a value
of $\gamma^*(0)$ significantly less than $4mJ/K^2.mole$. Measurements from other laboratories do not
provide the values of $n_1$ and $n_2$ necessary to test the decomposition of $\gamma^*(0)$ into two
components, but five new measurements at LBL have been added to those of Fig. 6 and are
included in Figs. 7 and 8 where the two components are shown separately for greater clarity.
Figs. 7 and 8 represent a comparison of the new data with the old, based on the parameters
derived in the earlier analysis -- not a new analysis that includes the new data as well as the
old. The points for the two Zn-doped samples were included in the original analysis because the data for those samples fit all the relevant correlations. However, the larger
number of points for low values of $n_2$ (see Fig. 7) now emphasizes a discrepancy between
those points and an extrapolation from the low-$n_2$ points such as that represented by the
dashed line. A new analysis with the Zn-doped points excluded gives in addition to the $n_1$-
and $n_2$-proportional components, an intrinsic contribution, $\gamma_0\sim 2\ mJ/K^2\cdot$mole, which is to be
compared with an upper limit of less than $1mJ/K^2\cdot$mole from the original analysis. For that
reason, and for the perhaps more compelling reason that the directly measured minimum
$\gamma^*(0)$ remains in the vicinity of $4mJ/K^2\cdot$mole, the possibility of an intrinsic $\gamma_0$ must be
recognized.

If there is an intrinsic linear term, it is possible that YBCO is unique among high-$T_c$
superconductors in this respect, and that the linear term is associated with the Cu-O chains.
The existence of a linear term associated with the Cu-O chains in YBCO has already been
suggested, and its absence in other high-$T_c$ superconductors is consistent with existing data
on their specific heats. For both $(La, Sr)_2CuO_4$ and the Bi compounds there are no
impurity phases with large pseudo-linear terms that are expected to make significant
contributions to $\gamma^*(0)$, and the interpretation of the data is therefore much more
straightforward than for YBCO. In the case of $(La, Sr)_2CuO_4$ at least one sample has
shown a $\gamma^*(0)$ value less than $1mJ/K^2\cdot$mole, and a correlation of $\Delta C(T_c)/T_c$ with $\gamma^*(0)$
suggests that $\gamma^*(0)$ is zero for a fully superconducting sample; for the Bi compounds a
number of samples have shown $\gamma^*(0)$ values that are substantially less than $1mJ/K^2\cdot$mole,
and, within the experimental uncertainty, $\gamma^*(0)=0$ [9].
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REFERENCES


Table I. Volume fraction of superconductivity determined from $\Delta C(T_c)$, $f_s = \Delta C(T_c)/78T_c$; and from $n_2$, $f_s(n_2) = 1 - n_2/0.012$.

<table>
<thead>
<tr>
<th>Condition</th>
<th>$f_s$</th>
<th>$n_2$</th>
<th>$f_s(n_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>0.85</td>
<td>0.0023</td>
<td>0.81</td>
</tr>
<tr>
<td>After first quench</td>
<td>0.78</td>
<td>0.0036</td>
<td>0.70</td>
</tr>
<tr>
<td>After second quench</td>
<td>0.73</td>
<td>0.0037</td>
<td>0.68</td>
</tr>
<tr>
<td>After rapid cool 950-350°C</td>
<td>0.62</td>
<td>0.0038</td>
<td>0.68</td>
</tr>
<tr>
<td>After reconstitution</td>
<td>0.73</td>
<td>0.0032</td>
<td>0.73</td>
</tr>
</tbody>
</table>

FIGURE CAPTIONS

Fig. 1 The specific heat anomaly at $T_c$.

Fig. 2 Analysis of low-temperature specific heat into its components.

Fig. 3 Mutual proportionality of $d\gamma^*/dH$, $\Delta C(T_c)/T_c$ and $\Delta S$: Determination of relative values of $f_s$.

Fig. 4 Correlation of $f_s$ with $n_2$.

Fig. 5 Resistivity vs. temperature, before and after quench.

Fig. 6 Original analysis of $\gamma^*(0)$ into $\gamma_1n_1$ and $\gamma_2n_2$ components.

Fig. 7 $\gamma_2n_2$ component of $\gamma^*(0)$; original analysis, but with new data added.

Fig. 8 $\gamma_1n_1$ component of $\gamma^*(0)$; original analysis, but with new data added.
FIG. 2
FIG. 3

YBa$_2$Cu$_3$O$_{7-\delta}$

$\Delta C(T_c)/T_c$, $d\gamma^*/dH$, $\Delta S$ (arb. units)

$F_s$ (arb. units)
YBa$_2$Cu$_3$O$_{7-\delta}$

$\nabla$ Zn Doped

$\begin{align*}
\frac{n}{\text{mole Cu}^{2+}/\text{mole YBCO}}
\end{align*}$

FIG. 4
FIG. 5

- As Received
- After Quench

Resistivity (arbitrary units)

Resistivity

T (K)

0.15
0.10
0.05
0.00

0.10
0.05
0.00

90 92 94 96 98
T (K)

200 250 300

XBL 9212-2570
Figure 6 shows a graph of the relationship between the specific heat capacity ($\gamma_1 n_1$, $\gamma_2 n_2$, $\gamma(O)$) and the dopant concentration ($n_1, n_2, n$) in YBa$_2$Cu$_3$O$_7$ samples. The graph includes data points and lines indicating the specific heat capacity increments with respect to the dopant concentration.

The graph includes markers labeled with numbers (1 to 9) corresponding to different samples, with a specific notation for Zn-doped samples. The x-axis represents the dopant concentration in moles/mole YBCO, while the y-axis represents the specific heat capacity in mJ/K$^2$·mole.
$\gamma_2 n_2$ (mJ/K$^2$.mole YBCO) vs. $n_2$ (moles $Cu^{2+}$ / mole YBCO)

- $YBa_2Cu_3O_{7-\delta}$
- Zn Doped
- New Data

$\gamma_0' + \gamma_2' n_2$

FIG. 7
\[ \gamma_1 n_1 \text{ (mJ/K}^2\text{.mole YBCO)} \]

\[ n_1 \text{ (moles Cu}^{2+}/\text{mole YBCO)} \]

YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta}

+ Zn Doped

O New Data

FIG. 8

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