Thermal expansivity below 300 K and low-temperature heat capacity of YBa$_2$Cu$_3$O$_7$

C. A. Swenson, R. W. McCallum, and K. No
Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011
(Received 30 May 1989)

Thermal expansivities from 1 to 300 K and heat capacities from 1 to 80 K are reported for three ceramic Y-Ba-Cu-O samples. The limiting Debye temperatures, $\Theta_D$, were found to be 322, 422, and 435 K for samples with (1) a few percent excess CuO, (2) high purity but large, elongated grains, and (3) high purity and small grains, respectively. A similar range of $\Theta_D$'s for superconducting samples is found in the literature, which suggests an insensitivity of superconductivity in ceramic Y-Ba-Cu-O to lattice properties (that is, to $\Theta_D$). The expansivity data for each of these samples showed scatter and instability just below $T_c$ and between 180 and 200 K, which, in general but not in detail, may be inherent to ceramic Y-Ba-Cu-O. The expected decrease in the expansivity on warming through $T_c$ was not unambiguously observed. The expansivity data suggest lattice softening below $T_c$, with, however, normal temperature dependences for the Debye $\Theta_D$'s and the Grüneisen parameters $\gamma$. The magnitudes and signs of the low-temperature expansivities and $\gamma$'s are characteristic of two sources for both the low-temperature “electronic” and “anomalous” contributions to the thermodynamic properties. The relatively small values for the lattice $\gamma$'s correspond to “normal” pressure dependences for the elastic constants of these materials, including the bulk modulus, and support the use of bulk moduli derived from x-ray measurements rather than from ultrasonic experiments.

I. INTRODUCTION

A number of unusual (often contradictory) features have been reported in ultrasonic, x-ray, heat capacity, and other data for the high-$T_c$ material YBa$_2$Cu$_3$O$_7$. These suggest possible phase transitions above $T_c$, hysteretic behavior, and very unusual elastic properties for ceramic samples. Linear thermal expansivity [$\alpha = (\partial \ln L / \partial T)_P$] measurements provide an additional probe which should reflect the same features as heat-capacity $(C_p)$ data, with the advantage that results can be obtained for both warming and cooling.

The present experiments combine complementary $\alpha$ and $C_p$ data to study three well-characterized and quite different samples of Y-Ba-Cu-O. The ratio, $\alpha/C_p$, can be normalized (see further) to obtain the dimensionless (roughly temperature-independent) Grüneisen parameter $\gamma$, which, as a measure of the anharmonicity of the system, provides an additional test of Y-Ba-Cu-O models. Published data for ceramic Y-Ba-Cu-O show considerable, apparently arbitrary variation from sample to sample, so Grüneisen parameters determined from measurements on the same sample should be more reliable than those determined from $\alpha$ measurements on one sample and $C_p$ measurements on another (see Vieira et al.).

II. EXPERIMENTAL DETAILS

The expansivities (1–300 K) were measured on both warming and cooling, with thermal cycling in regions where unusual behavior was observed. The differential capacitance dilatometer and associated instrumentation are similar to those of White and Collins, with modifications so that irregularly-shaped samples of arbitrary length can be measured. The system was calibrated using a standard copper sample. Capacitance and temperature readings for a data point were taken only with both were stable, with expansivities calculated from the differences between equilibrium values for successive data points. The time to change temperature varied from less than 1 min. at low temperature to 10 min. or more at the highest temperatures. Temperature increments (nominally $\Delta T = T/10$) ranged from 0.5 K at low temperatures and near $T_c$, to as much as 20 K above 200 K. Thermal equilibration times increased from a few minutes at the lowest temperatures to longer than 1 h above 40 K. The data scatter for these measurements on nominally 10-mm long samples varied from roughly 0.2% at high temperatures to a noise-determined low temperature limit of $5 \times 10^{-10}/$K. The absolute uncertainty of the results, which depends on the calibration and the capacitor plate area, is 1% (systematic) or $10^{-3}/$K, whichever is greater. The heat-capacity data for samples 2 and 3 were taken from 1.4 to 80 K with a conventional heat pulse calorimeter, with an accuracy of 1–2%. The maximum temperature for the heat-capacity data was determined by the upper limit of the germanium resistance thermometer calibration. The $C_p$ data for sample 1 were taken from 0.6 to 30 K using a different, less precise, calorimeter.

Results were obtained for three samples of superconducting Y-Ba-Cu-O, each of which was “single phase” as defined by x-ray analysis. Each had a relatively narrow superconducting transition region and $T_c$ above 90 K. Sample 1 was measured earlier, and was state of the art at the time. Subsequent analysis of this material using differential thermal analysis (DTA) suggests an excess of CuO (less than 2% in the sample) due to poorly controlled starting material. Sample 2 (a later sample) was
prepared after considerable refinements had been made in both starting material and processing. This sample was sintered in O₂ at 975°C, and had a relatively large (40 μm) maximum dimension for the elongated, randomly oriented grains and roughly 90% theoretical density. High-temperature hysteresis effects which were observed for this sample (see later), were tentatively ascribed to microscopic cracks at the grain boundaries, so sample 3 was prepared from the same starting material as sample 2, but was sintered at a lower temperature (925°C) to produce smaller (1 μm), relatively symmetrical, grains, and roughly 50% theoretical density. DTA analyses of samples 2 and 3 show much smaller impurity content than for sample 1, with less than 0.5% BaCuO₂ and CuO, and subtle differences which involve the distribution of these phases in the grain boundaries. These occur because liquid is present when sintering occurs at 975°C (sample 2), but is not present during sintering at 925°C (sample 3). The presence or absence of liquid determines the grain size and the density of the sample.

III. RESULTS AND DISCUSSION

A. General features

Figure 1 gives smooth overall α versus T relations for the three samples, as well as the scaled relation for a “normal” material, copper. The smooth relation for each sample was obtained from a somewhat arbitrary power-series fit to the data which provided a reference function against which several runs could be compared in detail. The differences between the data for the three samples are systematic and real. The shapes are similar, however, and the temperature dependence is quite different from that for copper. In particular, the ratio of the Y-Ba-Cu-O expansivity to that of copper in each case, has a minimum slightly below Tc (90 K), as is indicated (fortuitously) for sample 1 in Fig. 1, and is discussed in Sec. III C and Fig. 3 in the following.

The length of sample 1 was not stable above 245 K, making data taking impossible. The drift rate at 300 K (ΔL/L ≈ 10⁻⁴/k for the 7.3-mm long sample) was independent of the surrounding atmosphere (vacuum, 10⁻¹⁰ Torr helium or oxygen), and, since it reversed sign to an expansion below 270 K, was inherent in the sample. No room-temperature length drifts were observed for either samples 2 or 3. The data for samples 2 and 3 showed considerable scatter and hysteresis on temperature cycling above 180 K (see further), and all three samples showed length drift near 80 K as data were taken on the initial cool down. These effects, however, disappeared after the sample was warmed above Tc. The only other instances of sample instability in an expansivity measurement have been those by Lang et al., and Sparm et al., who could not obtain expansivity data between 30 and 60 K.

The spread in the values of the expansivities for our three samples is characteristic of the differences found in the literature. Our lowest value at 300 K, 11.5 × 10⁻⁴/K for sample 3, can be contrasted with 300-K values of 12.2 from White et al., 14.0 from Lang et al., and Sparm et al., 14.6 (extrapolated) from du Tremolet de Lacheisserie et al., 13.3 from Salomon et al., and roughly 20 (extrapolated) from Bayot et al., all in units of 10⁻⁴/K. Data given by Kadowaki et al. and Basargin et al. are comparable with these. This relative spread in high-temperature expansivities is similar to the relative spread in room-temperature heat capacities which has been reported by Junod et al., who conclude that the smallest 300-K heat capacities are associated with their “best” samples. By this criterion, sample 3 is our “best” sample.

Low-temperature data (see further) confirm that sample 1 is a very different material from samples 2 and 3. The differences in the αs of these latter two samples could be due to the highly anisotropic thermal expansion of Y-Ba-Cu-O which is observed in the x-ray measurements of Horn et al. and You et al. They report that the relative linear expansion from 100 to 300 K is roughly 2 times greater along the c axis than in the a-b plane of this orthorhombic material. The calculated relative length change from 100 to 300 K for a polycrystalline sample from these data (0.217% or 0.198%, with arithmetic or geometric averaging) is significantly greater than that for sample 2 (0.175%) or sample 3 (0.186%). This suggests preferential grain orientation in our samples with the c axis perpendicular to the cylinder axis.

The present samples were studied most extensively in three temperature regions. The first, between roughly 200 and 250 K, is where unusual behavior has been reported in the past in ultrasonic, heat capacity, and x-ray experiments. The second, near Tc, is where α for the superconducting state is expected to be about 2% larger than that for the normal state (about 10⁻⁴/K, see Lang et al.). Ultrasonic experiments, in particular, have suggested that major changes in the thermodynamic properties occur in this temperature region. Finally, the combination of α and CP data at lower temperatures is used to attempt to answer questions about the inherent versus impurity properties of Y-Ba-Cu-O at low temperatures.

B. High-temperature data

Figure 2 shows for samples 2 and 3 the differences between the actual data and the smooth relations of Fig. 1.
for temperatures between 180 and 280 K. The scaled copper $\alpha$'s (Ref. 11) in each figure indicate that the fit relation is smooth. The solid curve in each case is for the initial cooling towards $T_c$ and shows data scatter of roughly 3% for sample 2 and 6% for sample 3. The data for sample 2 on the final warming from 1 K (run 6F) are very strange, with abrupt changes and hysteresis as the temperature of the sample was cycled. This bizarre behavior led to the decision to obtain data for a fine-grained sample. The data for sample 3 show similar structure on cooling (possibly because the cooling rate was slower, with smaller temperature decrements), but no hysteresis or scatter for data taken on the final warm up from 1 K. Both smooth relations show an inflection in their difference from the smooth copper relation (see Fig. 2) which occurs in the 200–240 K region. This is the region where Junod et al. see differences in the high-temperature heat capacities of different samples. This inflection point is apparent in Fig. 1 for sample 2, and resembles (on a much smaller scale) that for sample 1. The magnitude of the inflection for sample 3 is appreciably less, suggesting a systematic effect. The largest, relatively random, “jumps” in $\alpha$ in Fig. 2 (roughly $10^{-5}$K in magnitude) correspond to excess relative length changes of $10^{-3}$ (or 1000 Å) over a 10-K temperature interval. If systematic structural changes are occurring in this region, the volume changes must be of roughly this size. Large data scatter (but different in detail) occurred both for our large-grain sample 2 and for the small-grain sample 3, so grain size (and microscopic cracks in the large grains) and density do not appear to be important parameters. Ultrasonic results, however, are very sensitive to grain size, with hysteresis virtually disappearing for fine-grained samples.

C. Expansivity near $T_c$.

The plots in Fig. 3 for the data from 75 to 110 K are similar to those in Fig. 2. More structure appears below 100 K on the initial cooling (solid line, 1C) for samples 2 and 3 than for sample 1, but drift and instability (small discontinuous length changes) occurred for all three near 80 K. For sample 2, for instance, the abrupt increase in $\alpha$ on the initial cooling through 90 K (1C) was followed by instabilities which persisted from 83 to 78 K, but which disappeared after warming to 88 K. Data which were taken at small temperature increments through $T_c$ (2W) and, eventually, to 160 K were monotonic and smooth, with no significant change in $\alpha$ (but, perhaps, a change in slope) near 90 K. Data for the subsequent cooling run to 48 K (3C), the following warming run to 116 K (4W), and a few points taken prior to cooling to 4 K (5C) also were smooth, as were those for the following warming run to 116 K (4W) and a few points taken prior to cooling to 4 K (5C). No data were taken in this region on the final warm up (curve 6F in Fig. 2). There were no signs of sample instability after the initial cooling run, but the differences between the various runs on cycling are significant and not understood. The data for samples 1 and 3 show similar effects, with the impure sample 1 being better behaved, and sample 3 (with more extensive data) showing more ($\pm 4\%$) structure and variation on cycling.

An elementary thermodynamic relation uses the pressure dependence of $T_c$ ($dT_c/dP$) and the universally observed discontinuity in $C_p$ at $T_c$ ($\Delta C_p$) to be used to predict a change in the volume expansivity ($\Delta \beta$) at $T_c$.

$$\Delta \beta = (dT_c/dP)(\Delta C_p/T_c)(1/V_m).$$

Using $dT_c/dP = 7 \times 10^{-10}$ K/Pa, $\Delta C_p = -45$ mJ/g au K$^2$ (where au is an atomic formula unit, an average, Ref. 5), and $V_m = 1.045 \times 10^{-4}$ m$^3$/g au (see further), Eq. (1) predicts $\Delta \alpha = \Delta \beta / 3 = -10^{-7}$/K, or roughly a 2% effect for a true polycrystal. While a discontinuity of this magnitude has been reported by Lang et al. and Ruan et al. for Y-Ba-Cu-O and by Kadowaki et al. for GdBa$_2$Cu$_3$O$_7$, it is not systematically evident for any of the samples in Fig. 3. The large increase in $\alpha$ on the initial cooling for sample 2 (3%) was encouraging, but did not reproduce. The various sets of data taken on cooling for the small-grained sample 3 each show a change in slope near 90 K, with an appreciably smaller effect for the warming curves. This predicted discontinuity in $\alpha$ has not been observed in three other expansivity experiments, possibly because of sample differences or a lack of sensitivity. Basargin et al.
port a large expansivity increase above \( T_c \), but no effect at \( T_c \).

There are reports of structural changes in the region of \( T_c \). In spite of the structure of Fig. 3, the data are smooth to roughly \( \pm 5\% \), even for the small temperature increments. If the scatter in the data is to be ascribed to discontinuous length changes as the sample temperature is changed (due to structural effects), the corresponding magnitudes of the relative length changes involved, \( \pm 3 \times 10^{-7} \), are exceedingly small. Thus, our data are in agreement with the x-ray\(^{6,21}\) and neutron scattering results\(^2\) which show monotonic behavior, and do not support the existence of relatively large volume anomalies at \( T_c \).\(^{2,3}\)

### D. Low-temperature results

#### 1. General

The low-temperature heat capacity and thermal expansivity for a metal each are expected to be of the form

\[
C_p = B_1 T + B_2 T^3 + B_3 T^5 + \cdots = \sum_{n \text{ odd}} B_n T^n , \quad (2)
\]

\[
\alpha = A_1 T + A_2 T^3 + A_3 T^5 + \cdots = \sum_{n \text{ odd}} A_n T^n . \quad (3)
\]

The first-order terms (\( A_1 \) and \( B_1 \)) usually are associated with an “electronic” contribution (which should be zero for a superconductor), while the third-order terms (\( A_3 \) and \( B_3 \)) are the limiting “lattice” or Debye contributions. The Debye temperature \( \Theta_0 \) is proportional to \( B_3^{-1/3} \). For Y-Ba-Cu-O we have used the 666 g mass of a 13-atom formula unit in calculating \( C_p \) and \( \Theta_0 \).

Figures 4 and 5 contain \( (C_p \) or \( \alpha)/T \) versus \( T^2 \) plots of the present low-temperature data. From Eqs. (2) and (3), the vertical intercept and slope correspond to \( A_1 \) (or \( B_1 \)) and \( A_3 \) (or \( B_3 \)), respectively. The smooth “fit” curves are from least-squares power series fits [using odd powers of \( T \), Eqs. (2) and (3)] to the data from 5 to 20 K. Table I gives the first three parameters for each of these fits. The differences in the \( C_p \) data for the three samples in Fig. 4 and in the \( \alpha \) data in Fig. 5, are characteristic of differences in other published \( C_p \) (Ref. 5) and \( \alpha \) (Refs. 7,12-14, 26) data. The “anomalous” contributions (deviations from the fit relations) below 5 K \( (T^2 < 25 \text{ K}^2) \) are characteristic of many Y-Ba-Cu-O experiments.\(^5\) The coefficients for Eq. (2) in Table I are not changed significantly (2% for \( B_1 \), less than 1% for \( B_3 \)) when the fits (possibly with fewer parameters) include only the 5–10 K range. The higher-order terms were included to assure continuity with the higher-temperature data (see further). If only the 5–10 K data had been used in a two-parameter analysis of the \( C_p \) results (that is, straight lines in Fig. 4), the \( B_1 \)'s would have been roughly 20% smaller, and the \( \Theta_0 \)'s would have been decreased by 30 K. Significant low-temperature deviations occurred in each case when the fit region was extended below 5 K.

Figures 4 and 5 show systematic variations from sample 1 to sample 3, with the major differences in the magnitudes above 5 K associated with the “electronic” terms (\( A_1 \) and \( B_1 \)). A subtle difference between Figs. 4 and 5 is

![FIG. 3. Differences from the smooth relations of Fig. 1 \((\alpha - \alpha_{ave})\) of the expansivity data for the three samples for temperatures near \( T_c \). Differences for a scaled expansivity for copper are also shown for each sample. \( \Delta\alpha = \pm 1 \times 10^{-1}/K \) corresponds to roughly \( \pm 2\% \) of the smoothed value. \( C \) refers to data taken on cooling, \( W \) to data taken on warming, and \( F \) to the final warming run. The numbers refer to the order in which the runs were made.](image-url)
the (normal) concave curvature for \( C_p \) \((B_2 > 0)\) and the (abnormal) convex curvature for \( \alpha \) \((A_3 < 0)\). This appears to be an inherent property of Y-Ba-Cu-O, since the widely differing magnitudes of the \( \alpha \)'s for the three samples rule out a calibration problem. The \( \alpha \)'s for samples 2 and 3 are equal at 15 K (not shown), with \( \alpha \) for sample 3 being greater than that for sample 2 to 250 K (Fig. 1). In contrast, \( C_p \) for sample 2 always is greater than that for sample 3; by 6\% at 20 K and 2\% at 80 K.

The low-temperature anomalous contribution to \( C_p \) is well defined in each case, and decreases in magnitude (together with \( B_1 \) and \( B_3 \)) from sample 1 to sample 3. The increase in \( \Theta_0 \) from sample 1 to sample 3 is significant. As was mentioned earlier, the magnitudes of these effects and parameters are characteristic of those found in the literature.\(^5,20,26\)

The behavior of the \( \alpha \)'s is more complex and less well defined at low temperatures. Both \( A_1 \) and \( A_3 \) decrease from sample 1 to sample 3, with, however, \( A_1 \) positive for sample 1, roughly zero for sample 2, and definitely negative for sample 3. A detailed analysis suggests that the anomalous contribution is negative for sample 1 (approaches \(-2 \times 10^{-9} \) K\(^{-2}\)) at 1 K), is positive for sample 2, and is zero for sample 3. The data of Vieira et al.\(^7\) are similar in magnitude to those for sample 1, although, in contrast with \( C_p \) data on the same sample, they do not show an anomalous contribution. The low-temperature \( \alpha \)'s reported by White and his collaborators\(^14,27\) are intermediate between those for samples 1 and 2, with no mention of an anomalous contribution. The results of Lang et al.\(^12\) again are comparable in magnitude with ours, but show an anomalous contribution below 7 K which is similar to that for sample 1. The low-temperature \( \alpha \) data of Sparn et al.\(^13\) are "dominated by extrinsic effects."\(^13\)

**FIG. 4.** A \( C_p/T \) vs \( T^2 \) plot of the low-temperature \( C_p \) data for each sample [Eq. (2)]. The smooth relation represents a fit of Eq. (2) to the data from 5 to 15 K, with lower-order parameters given in Table I.

**FIG. 5.** An \( \alpha/T \) vs \( T^2 \) plot of the low-temperature \( \alpha \) data for each sample [Eq. (3)]. The smooth relation represents a fit of Eq. (3) to the data from 5 to 15 K, with lower-order parameters given in Table I.
### Table I

The various lower-order parameters for fits of Eqs. (2) and (3) to the data for the three samples above 5 K. The units are such that $C_p$ and $\alpha$ are obtained in units of mJ/gfK, and $10^{-3}$/K, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expansivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_1$</td>
<td>0.175</td>
<td>-0.0009</td>
<td>-0.0505</td>
</tr>
<tr>
<td>$A_5$</td>
<td>0.00551</td>
<td>0.00332</td>
<td>0.000270</td>
</tr>
<tr>
<td>$A_6$</td>
<td>$-2.8 \times 10^{-5}$</td>
<td>$-4.0 \times 10^{-6}$</td>
<td>$-2.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Heat capacity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_1$</td>
<td>28.4</td>
<td>8.20</td>
<td>5.74</td>
</tr>
<tr>
<td>$B_2$</td>
<td>0.756</td>
<td>0.347</td>
<td>0.3061</td>
</tr>
<tr>
<td>$B_3$</td>
<td>$3.5 \times 10^{-3}$</td>
<td>$5.08 \times 10^{-4}$</td>
<td>$7.57 \times 10^{-4}$</td>
</tr>
<tr>
<td>Parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Theta_0$</td>
<td>322 K</td>
<td>419 K</td>
<td>435 K</td>
</tr>
<tr>
<td>$\gamma_{anom}$</td>
<td>$-5 , (\pm 3)$</td>
<td>$5 , (\pm 5)$</td>
<td>0 $, (\pm 5)$</td>
</tr>
<tr>
<td>$\gamma_d$</td>
<td>3.5</td>
<td>-0.1</td>
<td>-5.0</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>4.13</td>
<td>5.50</td>
<td>5.00</td>
</tr>
<tr>
<td>$\gamma_{tot}$</td>
<td>1.42</td>
<td>2.06</td>
<td>2.26</td>
</tr>
</tbody>
</table>

### 3. Grüneisen parameters

Experimentally, $C_p$'s and $\alpha$'s are found to have very similar temperature dependences. This can be understood in terms of the simple Mie-Grüneisen model\(^6\) in which the entropy is written as $S(\Phi(V)/T)$, and the dimensionless Grüneisen parameter

$$\gamma = -\frac{d \ln \Phi}{d \ln V} = \frac{\beta B_T}{(C_p/V)}$$

is defined in terms of the volume thermal expansivity $\beta$, the constant volume heat capacity $C_p$, per unit volume, and the isothermal bulk modulus $B_T$. Hence, $\Phi$ gives the energy scale in this model and $\gamma$ its volume dependence. A $\gamma$ can be defined for the bulk material, or, more appropriately, $\gamma$'s can be defined for each of the three "independent" contributions (anomalous, electronic, lattice) to the low-temperature thermodynamics of Y-Ba-Cu-O. These $\gamma$'s are defined as

$$\gamma_{tot} = (3B_T/V)(\alpha_{tot}/C_{Ptot})$$

### 2. $C_p$'s and the Debye function

At higher temperatures, the direct display of both $C_p$ and $\alpha$ is difficult because of their rapid temperature dependence. The Debye function,$^{28}$ $D(\Theta/T)$, gives a reasonable approximation to the temperature dependence of heat capacities, and can be used in a number of different ways to normalize $C_p(T)$. A common procedure is to choose the value of $\Theta$ which, when used with the Debye function and the experimental temperature, will give the experimental $C_p$ for a data point [$C_p(T) = D(\Theta(T)/T)$]. In practice, this will apply only to the lattice heat capacity, with $C_p_{lat}(T) = C_p - B_1T$.

Figure 6 contains this representation of the $C_p$ data for each of the present samples, together with that for the smooth relation for these data (identical with that in Table I at low temperature). While the general features of these curves (above 10 K) are independent of the parameters in Table I, the low-temperature shapes and $\Theta_0$'s depend on the values of $B_1$ that are used. In particular, a change in $B_1$ of $\pm 1$ mJ/gfK$^2$ will change $\Theta_0$ by $\pm 1\%$. The scatter in the data for sample 3 at 65 K represents difficulties in data taking which could be sample related.

The general features of the curves in Fig. 6 are quite normal.$^{28}$ The rapid decrease of $\Theta(T)$ with increasing temperature (approximately 20%), to a minimum value at roughly $\Theta_0/15$ is the result of dispersion in the density of states ($B_2 >0$), while the subsequent increase with temperature also is normal. The present "lattice" contribution is defined in terms of the low-temperature electronic contribution (Table I). Analyses of the jump in the heat capacity at $T_c$ generally give a significantly larger electronic contribution which, in turn, is used to define the lattice heat capacity above $T_c$.\(^{29}\) It is unfortunate that our data do not extend into the normal-state region.

![FIG. 6](image-url)

The temperature dependence of an equivalent Debye $\Theta$ for the three samples. See the text for details.
\[ \gamma_{\text{anom}} = (3B_T V)(\alpha_{\text{anom}} / C_P \text{anom}) \]
\[ \gamma_{\text{elect}} = (3B_T V)(\alpha_{\text{elect}} / C_P \text{elect}) \]
\[ = (3B_T V)(A_1 / B_1) \]
\[ \gamma_{\text{latt}} = (3B_T V)(\alpha_{\text{latt}} / C_P \text{latt}) \]
\[ = (3B_T V)(A_3 / B_3) \]

where for polycrystalline Y-Ba-Cu-O, \( \beta = 3\alpha \), \( C_P = C_P \text{latt} \) at low temperatures, and \( B_T \) and \( V \) vary only slowly with temperature. The right-hand side of Eqs. (6) and (7) uses the notation of Eqs. (2) and (3) to give limiting values. Since the Debye model applies rigorously at low temperatures, the limiting value of

\[ \gamma_{\text{latt}} = \gamma_0 = -d \ln \Theta_0 / d \ln V \]

and is a function of the pressure dependence of the elastic constants.

Significant discrepancies exist \( \text{between values of the bulk modulus for ceramic Y-Ba-Cu-O which are derived from ultrasonic measurements (65 GPa or 650 kbar) and from high-pressure x-ray experiments (100–180 GPa). Partly because our results are independent of grain size and sample density, but more so for reasons which are given later, we have chosen to use a (microscopic) x-ray value of } B_T \text{ (180 GPa) (Ref. 31) in our calculations. Similarly, we have used the (microscopic) ideal molar volume from the x-ray lattice parameters, } 1.05 \times 10^{-4} \text{ m}^3/\text{g au}\text{ rather than the bulk density. Thus, the common factor in the definitions of } \gamma \text{ in Eqs. (4)} \text{–(7) is given by } 3B_T V = 5.67 \times 10^7 \text{ J/g au}. \text{ If } \alpha \text{ and } C_P \text{ (as in Table I) are measured in units of } 10^{-8} /K \text{ and } \text{mJ/g au K}, \text{ respectively, this common factor becomes 567. The results of the } \gamma \text{ calculations are shown in Table I for the low-temperature limit for all three samples, together with the high-temperature } (T > 20 \text{ K}) \text{ limiting value of the lattice } \gamma \text{, } \gamma_{\text{inf}}, \text{ which follows from Fig. 7. If the smaller x-ray or ultrasonic } B_T \text{ had been used, the magnitudes of the } \gamma \text{'s in Table I, and the following, would be divided by 1.8 or 3, respectively.}

The differences in the magnitudes of the coefficients in Table I disappear to a great extent when } \gamma_{\text{elect}} \text{ is calculated. The signs of the } \gamma \text{'s in Table I reflect the sign of the } \alpha \text{ contribution, since } C_P \text{'s always must be positive. While } \gamma_{\text{elect}} \text{ and } \gamma_0 \text{ are given by the right-hand sides of Eqs. (6) and (7), respectively, } \gamma_{\text{anom}} \text{ is much more uncertain, since it is calculated explicitly from } \alpha \text{ contributions (Fig. 5), which show much more scatter than do the } C_P \text{ data (to a good approximation, } C_P \text{ is constant for each of the three samples).}

Figure 7 gives the temperature dependence of } \gamma_{\text{latt}} \text{ [Eq. (7)] and of } \gamma_{\text{tot}} \text{ [Eq. (4)]}. \text{ Here, } C_P \text{ (} C_P \text{ lat} = C_P - B_1 T) \text{ is calculated from a smooth relation (Fig. 6), while for } \alpha \text{ (} \alpha_{\text{lat}} = \alpha - A_1 T) \text{, both the actual data (•, +) and a smooth relation (−−) are used. The scatter of the data points for } \gamma_{\text{tot}} \text{ shows directly the precision of the data, while the low-temperature scatter for } \gamma_{\text{latt}} \text{ is much enhanced due to the subtraction of the "electronic" terms.}

In Fig. 7, the relatively rapid decrease in } \gamma_{\text{latt}} \text{ with increasing temperature reflects the different signs for } A_3 \text{ and } B_3 \text{ in Table I. This behavior is less pronounced for } \gamma_{\text{tot}} \text{ because of the electronic contributions to } \alpha. \text{ The constancy of } \gamma \text{ above } 20 \text{ K (} \gamma_{\text{inf}} \text{ in Table I) is somewhat surprising, since this occurs for most solids above roughly } T = \Theta / 5 (= 80 \text{ K}). \text{ The differences between samples 2 and 3 are not significant, although the smaller values of } \gamma \text{ for sample 1 probably represent a qualitative difference. If the smallest heat capacities of Junod et al. are used with our expansivities for sample 3 (Fig. 1), } \gamma \approx 2.3 \text{ from 80 to 300 K.}

The differences in the } C_P \text{'s in Fig. 4 (see the heat capacity parameters in Table I) are systematic, with the smaller electronic and lattice terms corresponding to smaller anomalous contributions. The } \alpha \text{ results (Fig. 5), however, reveal significant differences between the samples. If the behavior of the pure material were to be that of the "lattice," with the low-temperature differences due only

---

**FIG. 7.** The temperature dependence of the “lattice” and total Grüneisen parameters for the three samples. See the text for details.
to different levels of a “common impurity,” $\gamma_{\text{anom}}$, and $\gamma_{\text{el}}$, would be sample independent, which they are not. The differences in the nonlattice $\alpha$’s (and $\gamma$’s) for these samples are significant, and suggest either a minimum of two distinct dominant impurities, or “anomalous” and “electronic” contributions which are inherent to both the pure material and to the “impurity.” This is qualitatively evident in the $\gamma_{\text{tot}}$ plots in Fig. 7, since these are independent of an arbitrary separation into various contributions.

4. Bulk modulus comments

Collocott et al.\textsuperscript{27} and Cankurtaran et al.\textsuperscript{30a} have discussed the discrepancy between ultrasonic and x-ray diffraction determinations of the bulk modulus for ceramic Y-Ba-Cu-O. The ultrasonic results, even after corrections for porosity using a scattering model, suggest a material which is elastically quite soft,\textsuperscript{30} while the x-ray results\textsuperscript{31–33} are typical of ceramic oxides. The differences may be due to porosity, grain boundaries, and/or microcracks in the samples used for the ultrasonic measurements, or may demonstrate an inherent difference between the atmospheric pressure and very-high-pressure properties of ceramic Y-Ba-Cu-O. The pressure-dependent ultrasonic results\textsuperscript{30} show that the $P=0$ elastic constants (particularly $C_{11}$ and the bulk modulus) increase rapidly with pressure. The bulk modulus resulting from the data and the corrections\textsuperscript{30a} increases rapidly from a relatively low value ($\approx 65$ GPa), and extrapolates to the larger values required to give agreement with x-ray data\textsuperscript{1–3} at diamond anvil cell (DAC) pressures (6–15 GPa). In this case, $(dB_{T}/dP)_{P=0}=85$, while for most solids, $dB_{T}/dP$ has values between 3 and 7. The low value for $B_{T}$ and its abnormal dependence on pressure are postulated to reflect the inherent vacancy structure of superconducting Y-Ba-Cu-O,\textsuperscript{30} and, presumably, also should be characteristic of the crystal.

The lattice Grüneisen parameters also provide an indication of the pressure dependence of the elastic constants, since their magnitudes are related directly to the pressure dependence of the elastic constants.\textsuperscript{4} A comparison of 295 K thermal $\gamma$’s [Eq. (4)] and those calculated from the pressure dependences of the elastic constants shows a very large difference [0.8 from Eq. (4) versus 12–24, dependent on the sample] which is not explained. Our high-temperature results for samples 2 and 3, in contrast with the ultrasonic work, show a small, if any, grain size or density dependence, and should be characteristic, at least to a first approximation, of the bulk crystalline material. The lattice $\gamma$’s in Table I and Fig. 7, give no indication at any temperature of the extreme volume sensitivity which is suggested by the high-pressure ultrasonic work.\textsuperscript{30} The low-temperature values are particularly important ($\gamma_0$ in Table I), since they are related most directly to the high-pressure ultrasonic results. For a direct comparison with the published calculations, the present $\gamma$’s must be reduced in magnitude (divided by 3) because of the different $B_{T}$’s which were used.

Our conclusion is that the x-ray measurements provide the best available values of the bulk modulus for ceramic Y-Ba-Cu-O, and, presumably, for single crystals also. The “correct” x-ray value is not well established, since Fietz et al.\textsuperscript{31} find $B_{T}=180$ GPa in DAC measurements to 14 GPa, while Takahashi et al.\textsuperscript{32} and Jaya et al.\textsuperscript{33} obtain $B_{T}=100$ GPa in experiments to 6 GPa.

IV. Conclusions

A. General comments

The following discussion applies only to the present data which are compared with selected published results. Standard samples of ceramic Y-Ba-Cu-O do not exist, and reported properties of carefully prepared and well-characterized samples often are quite different. The range in (reliable) reported values of $\Theta_0$, for instance, suggests differences in 10-K lattice heat capacities of almost 100%. We observed relaxation effects in thermal expansivity and heat-capacity measurements which mandate extreme care in establishing equilibrium conditions. Our expansivity data, in particular, are not complete, since we cannot state (due to a lack of time) that these samples would have behaved in the same manner upon a second cooling from 300 K. A major conclusion is that the thermal expansivity of Y-Ba-Cu-O (or even of a sample of ceramic Y-Ba-Cu-O) is not a well-defined quantity. The differences in the x-ray compressions\textsuperscript{31–33} may be experimental in origin, or could be real and reflect a difference in elastic properties similar to that which appears in the $\Theta_0$’s. Insofar as possible, as many different types of data should be taken on a given sample over as wide a temperature range as possible to establish common relationships. Our determinations of $\gamma$ (Fig. 7), for instance, show a common temperature dependence, with absolute values which depend on the $B_{T}$ that is used. To be complete, the pressure dependence of $T_c$ should have been determined for our samples, as well as $\Delta C_p$ at $T_c$, to verify (or show an exception to) Eq. (1). Until the reasons for significant differences between samples prepared in different laboratories are determined, it should be recognized that, although careful measurements may characterize precisely a given sample, there is no certainty that the results will apply to a “true” superconducting ceramic Y-Ba-Cu-O sample, when it is prepared.

B. Impurity effects

Each of the present samples showed a sharp magnetic superconducting transition near 90 K, and was “x-ray pure,” with no evidence for the presence of a second phase. Most low-temperature heat-capacity data for Y-Ba-Cu-O resemble those in Fig. 4, with a finite $B_1$ term and an “anomalous” contribution which is a function of magnetic field.\textsuperscript{5} Qualitatively, the present $C_p$ data fit into a picture where the magnitude of the linear coefficient ($B_1$) correlates with the anomalous contribution. The nonsystematic sample dependences of $\gamma_{\text{anom}}$ and $\gamma_{\text{el}}$ in Table I, however, suggest that at least two independent impurities contribute to the low-temperature differences for these samples, or that “electronic” (linear in $T$) and “anomalous” terms are common to both the “pure” material and to the major impurity if, indeed, it is common
to all three samples.

A striking result is the very large effect on the thermodynamic properties of only a few percent of excess CuO. Figures 1 and 6 show that both the thermal expansivity (to 240 K) and the heat capacity (to 30 K) are much larger for the slightly impure sample 1 as compared with the higher quality samples 2 and 3. Although the expansivity of sample 3 is slightly greater than that for sample 2 at most temperatures, the existence of a slightly increasing slope for this sample near room temperature (Fig. 1) suggests that sample 3 is more likely to be characteristic of the “ideal” material.

The systematic increase of $\Theta_0$ from sample 1 to sample 3 suggests a correlation which has not been commented on previously. Unfortunately, this correlation is not obvious in the review of Fisher et al.,24 nor in the papers where a series of samples have been prepared systematically. These include Ecket et al.,25 where samples characterized by Junod et al.,26 were used, and Collocc et al.26 A striking feature of these and other25–37 results with high-purity samples, is that a reasonably small value of the linear heat-capacity coefficient $B_1 = 5.1 \pm 1$ mJ/ g au K$^2$, and a small anomalous contribution to the heat capacity (ranging from 25% of that for sample 3 in Fig. 4 to, effectively, zero) can occur with values of $\Theta_0$ as small as 371 K (Refs. 36 and 37) and as large as 440 K.26,25 Other data suggest that $\Theta_0$ can be as small as 325 K (sample 1) or 345 K (Ref. 7) and as large as 465 K (Ref. 38) for superconducting Y-Ba-Cu-O. Recent unpublished results from this laboratory for a magnetically pure Y-Ba-Cu-O sample29 showed a much reduced anomalous contribution when compared with sample 3 ($T^3$ dependence to 2.5 K), a linear coefficient $B_1 = 5.70$ mJ/g au K$^2$, and $\Theta_0 = 456$ K. While some of these differences (approximately 10%) may be associated with analysis techniques (compensation of the anomalous contribution, the upper limit of $T^3$ behavior, etc., see the discussion in III D), this does not appear to be the case for the present results and those cited above.26,35–37

This wide range of $\Theta_0$'s for samples which have been prepared in roughly the same manner and which show identical superconducting behavior is characteristic of considerable differences in lattice properties, differences which are difficult to ascribe to trace impurity effects. The question as to whether or not the linear term in $C_P$ is an inherent property of ceramic Y-Ba-Cu-O appears to have a positive answer.26,40 Additional questions are, first, why do lattice properties ($\Theta_0$'s) appear to have so small an influence on superconductivity in ceramic Y-Ba-Cu-O and, second, what is responsible for these differences in lattice properties for “good” samples?

C. Nonequilibrium effects

The existence of regions of hysteresis and sample instability for our three samples is a result which might apply to all ceramic Y-Ba-Cu-O samples. The length of sample 1 was unstable for temperatures above 240 K, and showed time-dependent changes which reversed sign near 270 K. The expansivity data for each of our samples (Figs. 2 and 3) showed unusually large data scatter on both the initial cooling and upon warming for temperatures from roughly 250 to 180 K, and also length drifts and jumps upon an initial cooling to 80 K, with no obvious pattern to the behavior. These regions of “instability,” which also showed hysteresis on thermal cycling, suggest that our samples were not in a true equilibrium state. This behavior does not depend qualitatively on crystal size, nor on bulk sample density, since sample 2 had both larger grains (elongated 40 µm versus 1 µm) and a much larger density (90% theoretical versus 50%) than sample 3. The origins of these “high-temperature” effects, which have been observed in one form or another in many different experiments,1–3,5,22,41 are not clear. They could be due to inherent structural effects in Y-Ba-Cu-O (with extremely small volume changes), to micro-cracks in the samples (which, however, should not be present in our small grain sample 3), or to trace impurities. Slasky et al.7 argue that the high-temperature heat-capacity anomalies they have observed (180–250 K) cannot be due to CuO in their samples. Our samples 2 and 3 likewise should be free of CuO.

D. Bulk thermodynamic properties

Outside of questions about the magnitudes of $\Theta_0$ (see Sec. IV B), the temperature dependences of the equivalent Debye temperatures (Fig. 6) and $\gamma$’s (Fig. 7) are similar to those of other solids.6,28 The magnitudes of the lattice $\gamma$’s are “normal” and roughly the same (Table I), in spite of uncertainties in the bulk modulus, and do not provide immediate clues as to the nature of superconductivity in Y-Ba-Cu-O.27 The rapid decrease in $\gamma$ with increasing temperature (Fig. 7) reflects the (usual) different signs for the “dispersion” terms $B_1$ and $A_1$, in Eqs. (2) and (3). A comparison between the expansivities of these Y-Ba-Cu-O samples and those of a “normal” material, copper, shows that the ratio $\alpha_{Y-Ba-Cu-O}/\alpha_{Cu}$ has a minimum just below $T_c$, as is shown (fortuitously) for sample 1 in Fig. 1, and more quantitatively in Fig. 3. This suggests a general change in lattice properties as $T_c$ is approached, with the solid becoming relatively “softer” in an elastic sense as it is cooled through $T_c$. Ultrasonic data, which are not normalized to a standard substance, are quoted as suggesting a hardening of the lattice in this region.5

E. $\Delta \alpha$ at $T_c$

Figure 3 shows no systematic evidence for any of our samples of the decrease in $\alpha$ on warming through $T_c$ ($\Delta \alpha = 10^{-7}$/K), which is predicted by thermodynamics [see Eq. (1)]. This effect is “obvious” (but too large) only for the initial cooling of sample 2, and can be deduced from only selected runs for sample 3. Indeed, the only clear signal of $T_c$ for samples 2 and 3 (more so for sample 3) is an almost universal change in the slope of the $\alpha$ versus $T$ relation near 90 K. Three studies, however, on Y-Ba-Cu-O (Refs. 12 and 24) and Gd-Ba-Cu-O,18 have clearly resolved this effect.

The highly anisotropic structure of Y-Ba-Cu-O may offer an explanation for what appear to be sample-dependent results for $\Delta \alpha$. In contrast with the discontinuity in $C_P$, the magnitude of the change in $\alpha$ at $T_c$ for
a single crystal will be orientation dependent, and a proper thermodynamic description will involve a correlation with uniaxial stresses. This suggests potential difficulties in understanding quantitatively the pressure dependence of $T_c$ for a ceramic polycrystal, since the stresses need not be uniform. Recent experiments by Koch et al.\textsuperscript{42} suggest that the pressure dependence of $T_c$ for single crystal Y-Ba-Cu-O has the opposite sign from that for ceramic samples. A systematic study of the pressure dependence of $T_c$ for carefully-prepared samples of different grain sizes, as well as for single crystals, would be very useful. The dependence of $T_c$ on $c$ axis stress\textsuperscript{43} has been shown to be consistent with $dT_c/dP$ measurements.\textsuperscript{43}

F. Ultrasonic versus x-ray bulk moduli

The relatively small (and “normal”\textsuperscript{6}) magnitudes of the lattice Grüneisen parameters (Table I, Fig. 7) suggest that the elastic constants for ceramic Y-Ba-Cu-O have a normal pressure dependence. This is in contrast with the results from high-pressure ultrasonic experiments,\textsuperscript{30} which suggest at least an order-of-magnitude larger pressure dependences for the elastic constants. We cannot reconcile their conclusions and our results, and have decided that the bulk modulus from high-pressure x-ray experiments is more consistent with our data.

Note added in proof: H. Ledbetter [Physica C \textbf{159}, 488 (1989)] uses arguments which involve ultrasonic data, comparisons with other materials, and expected magnitudes for $\gamma$ to suggest that the bulk modulus for Y-Ba-Cu-O should be closer to 100 GPa than the maximum x-ray value, 180 GPa, which is used in the calculations in this paper.

ACKNOWLEDGMENTS

The authors are indebted to Dr. Robert N. Shelton for assistance with sample 1, and to Dr. H. D. Yang for the $C_p$ measurements on this sample, and to J. E. Ullman for carrying out the DTA analyses. We also acknowledge useful discussions with Professor J. D. Verhoeven. This work was performed at the Ames Laboratory, Iowa State University and was supported by the Director of Energy Research, Office of Basic Science, U.S. Department of Energy under Contract No. W-7405-ENG-82.


\textsuperscript{9}M. Slatski, T. Laegred, O. M. Nes, and K. Fosheim (unpublished).


\textsuperscript{19}A. Junod, A. Bezinge, and J. Muller, Physica C \textbf{152}, 50 (1988).


39W. Lee and D. C. Johnston (private communication).
40S. E. Stupp and D. M. Ginsberg, Physica C (to be published).