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Thermal Expansion of High-T_c Superconductors[1]

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Measurements are reported of the linear thermal expansion of polycrystalline samples of BiCaSrCu oxide and BiPbCaSrCu oxide from 2 K up to about 1000 K. The measurements are compared with our earlier data on LaSrCu oxide and YBaCu oxide materials and are found to be similar in magnitude at normal temperatures. Near the superconducting transition temperature T_c, anomalies in the linear coefficient $\alpha(T)$ are small and similar in relative magnitude to those observed in the heat capacity.

KEY WORDS: high-T_c; superconductivity; thermal expansion.

1. INTRODUCTION

The present measurements on the thermal expansion of BiSrCaCu oxide (BSC) and BiPbSrCaCu oxide (BPSC) superconductors were made for three purposes:

(i) to provide technical data on the average expansion coefficient of bulk polycrystalline material over a wide temperature range, which would be useful in designing structures involving such material;

(ii) to measure the magnitude of anomalies in the linear coefficient of thermal expansion α in the vicinity of the superconducting transition temperature, T_c, as a guide to the nature of the interactions; and

(iii) to obtain data on the temperature dependence of α at liquid helium temperatures which are of basic interest.

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Previously we reported measurements on a $La_{1.85}Sr_{0.15}CuO_4$ (LS) sample and various $YBa_2Cu_3O_7$ (YB) samples [1, 2] which showed the following characteristics.

(i) $\alpha(T)$ has a form below 500 K similar to the temperature dependence of the heat capacity at constant pressure, except that a "knee" is observed in LS above 200 K. Above 500 K there is structure in the length change curves or $\alpha(T)$ which can be attributed partly to oxygen movements [3]. The magnitudes of $\alpha(T)$ near room temperature are generally comparable to or up to 20% larger than for ceramic oxides such as MgO, cubic zirconia, and $SrTiO_3$.

(ii) Near T_c, which is ca. 32 K for the LS and 91 K for the YB sample, small changes in slope of $\alpha(T)$ can be seen by plotting α/T or α/T^2. They are similar to the changes in heat capacity, C.

(iii) At liquid helium temperatures, there is evidence of a linear (T–) term in $\alpha(T)$ which can be identified with electronic contributions from a nonsuperconducting phase and/or with tunneling states in a disordered defect structure. Note that in nearly all observations of heat capacity of these materials, there is evidence of a linear term which is, however, partially masked by a Schottky bump arising from chemical impurities or a magnetic phase [4, 5].

Figure 1 illustrates the spread of 10–20% in our values for the four different YB samples. The values do not correlate with density so we assumed that they represent varying degrees of preferred orientation. The large anisotropy of expansion between the c axis and the a, b axes (or ab plane) is shown clearly by the points taken from X-ray data of You et al. [6]; $\alpha_c \simeq 2 \times \alpha_a$.

The average $\bar{\alpha} = (\alpha_a + \alpha_b + \alpha_c)/3$ from [6] is about 10% larger than our top values (on YB25) or than data of Lang et al. [7]. We have not included the values of Salomons et al. [3], which extend up to 500 K and are similar to our data above 200 K but are significantly larger around 100 K.

Lang et al. [7] studied α with particular care in the vicinity of T_c for both LS and YB and showed that α/T decreased by about 2% on warming slowly through the transition. This decrease was similar to the anomaly in the heat capacity, C_P.

Below about 7 K, Vieira et al. [9] found that α for their YB samples could be represented by $\alpha = aT + bT^3$, with $a \approx 1.03 - 1.36 \times 10^{-9}$ in K^{-2}, in fair agreement with our values of 0.9, 1.3, and $1.5 \times 10^{-9}\,K^{-2}$.

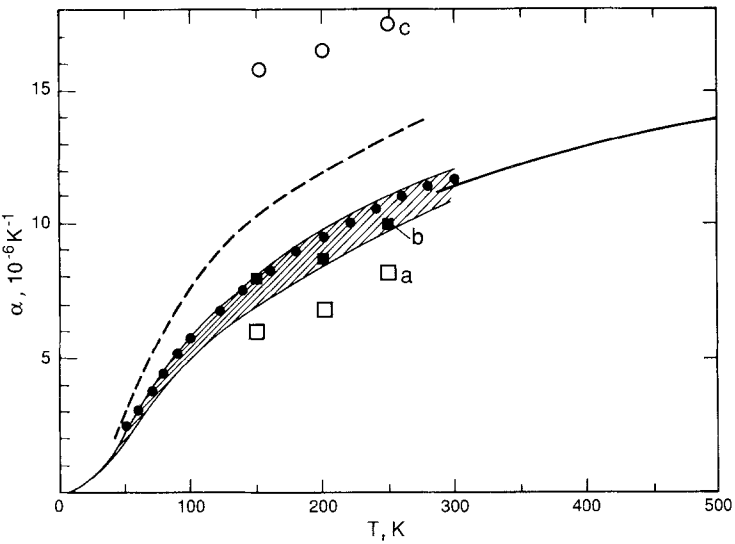

Fig. 1. Linear thermal expansion coefficient, α, for $YBa_2Cu_3O_7$. (——) YB18 from White et al. [2]; shaded area shows spread of values for four samples. (●) Ref. 7; (---) Ref. 8; (□, ■, ○) X-ray values for *a*, *b*, and *c* axes [6].

There have been fewer thermal measurements on the BSC system, due partly to its later discovery and to the presence of more than one superconducting phase. Heat capacity measurements at low temperature indicate a T^3 term with a corresponding Debye temperature of about 260 K [10, 11] (cf. $\Theta_0 \sim 420$ K for YB samples [4]) but with some uncertainty about a linear term. We have not found published expansion data for these BSC materials.

2. MEASUREMENTS

The samples (see Table I) were made by standard solid-state reaction techniques, starting from Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO powders.

Table I. Characteristics of Specimens

Sample	Nominal composition	T_c (K) (zero resistance)	Density ($g \cdot cm^{-3}$)
BSC26	$Bi_{2.1}Sr_2CaCu_2O_8$ (2212)	75[a]	4.81
BPSC6	$Bi_{1.8}Pb_{0.3}Sr_2CaCu_2O_8$ (2212)	89	4.56
BPSC8	$Bi_{1.6}Pb_{0.4}Sr_2Ca_{2.5}Cu_{3.5}O_8$ (2223)	106	5.10

[a] Broad transition, T_c (onset) $\sim$ 95 K, strong Meissner effect at 77 K.

Those denoted by BSC26 and BPSC6 were sintered at 865 and 855°C, respectively, and quenched in liquid nitrogen. Both were predominantly single-phase 2:2:1:2 materials (as indicated by X-ray diffraction), the lead-substituted sample showing a much sharper T_c transition. The sample BPSC 8 was sintered at 860°C for 60 h and contained at least 90% 2:2:2:3 phase, with the 2:2:1:2 phase as the major impurity. Rods of 6-mm diameter were made by bidirectional uniaxial pressing.

The ends of the cylinders, each about 20 mm long, were ground flat and parallel. Each was mounted in a copper three-terminal capacitance dilatometer [12] (containing a low pressure of helium gas), where the linear thermal expansion was measured between 293 and 273 K and then from 130 down to 2 K. These measurements of length change were made with an uncertainty of $\sim 10^{-9}$ cm below 10 K and $\sim 10^{-8}$ cm above 10 K. Temperatures were measured by Ge or Pt resistance thermometers calibrated in this laboratory.

Later each sample was placed in a push-rod dilatometer (Adamel Lhomargy, France) and cycled from room temperature up to 975 K in air. During the first heating cycle, the dilatometer trace was "bumpy" (inflections) but appeared smooth and reproducible on further cycling. An exception was BPSC6, which fractured on its second heating above 600 K.

The T_c values in Table I were obtained by resistance measurements on duplicate samples from the same batches of material. For BSC26, the resistance transition was smeared out over the range 100–75 K, while the other two showed relative sharp transitions over an interval of less than 3 K.

3. RESULTS

Figure 2 shows individual values of α below 130 K measured in the capacitance dilatometer. An obvious feature is the inflection or knee near 60 K, the transition region between measurements with a liquid nitrogen bath ($T > 50$ K) and those with liquid helium ($T < 45$ K). We have not observed this with other materials so it seems unlikely to be an artifact of measurement and deserves further study. On some runs there were slow drifts in the apparent length near 50–80 K over periods of many minutes after temperature had become steady.

Figure 3 shows data below 15 K plotted as α/T versus T^2. There is no clear evidence of a positive intercept on the Y axis, which would indicate a T term comparable with that observed in LS and YB samples, for which $10^8\alpha$ may be approximately expressed as $0.1T$ plus a term of order T^3. Also puzzling is the negative curvature above 6 or 7 K, which is shown even more clearly by plotting α/T^3. Below 6 or 7 K, a T^3 dependence fits the

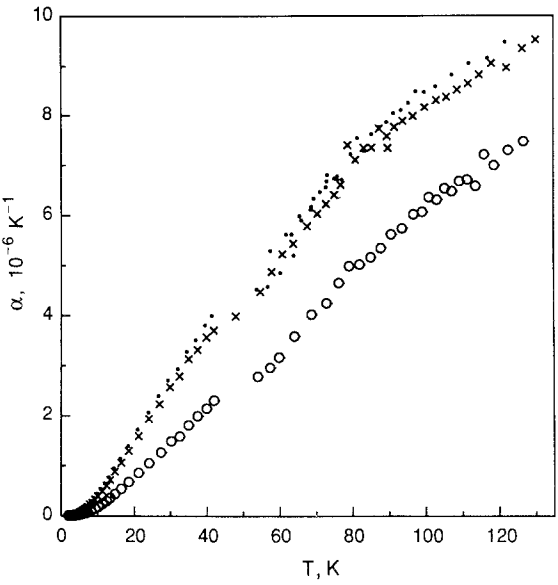

Fig. 2. $\alpha(T)$ below 130 K for BPSC6 (●), BSC26 (×), and BPSC8 (○).

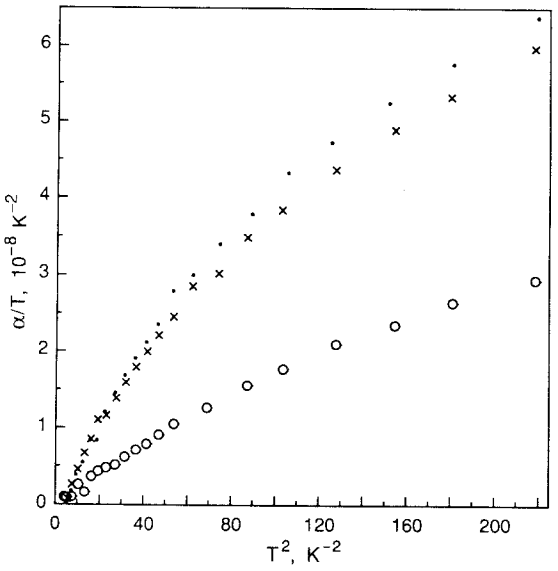

Fig. 3. α/T versus T^2 below 15 K; legend as for Fig. 2.

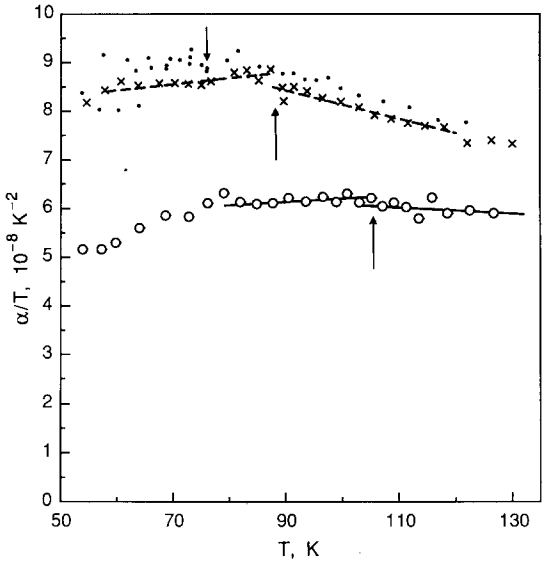

Fig. 4. α/T in vicinity of T_c. Arrows marked T_c as determined from zero electrical resistance; legend as for Fig. 2.

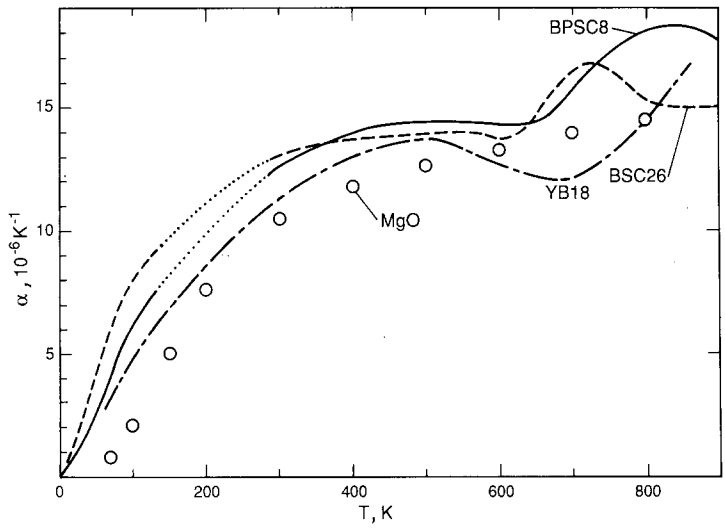

Fig. 5. $\alpha(T)$ for BSC26 and BPSC8 compared with YB18 [2] and MgO [13].

data within limits of error: $10^8\alpha \approx 0.05T^3$ in K^{-1} for BSC26 and BPSC6 and $10^8\alpha \approx 0.018T^3$ in K^{-1} for BPSC8.

In Fig. 4 we show α/T in the region near the superconducting transition T_c. In the case of BSC26, there is evidence of a discontinuity in α/T near 89 K of 2–3%. For BPSC8 ($T_c \approx 106$ K), we can see an apparent discontinuity more clearly by smoothing the length change values, $\Delta l(T)$, differentiating, and plotting α/T on an expanded scale. This indicates a jump $\Delta\alpha/T \approx 0.2 \times 10^{-8}\ K^{-2}$ or $\Delta\alpha \approx 0.2 \times 10^{-6}\ K^{-1}$ (or 3%).

For BPSC6, repeated measurements showed greater drifts and uncertainties, particularly below 80 K, and we could not estimate $\Delta\alpha/T$ reliably.

Finally, in Table II and Fig. 5, we show $\alpha(T)$ over a wider temperature

Table II. Smoothed Values of $\alpha(T)$ in Units of $10^{-6}\ K^{-1}$

T (K)	BSC26	BPSC6	BPSC8
4	0.035	0.031	0.014
6	0.105	0.110	0.042
8	0.225	0.245	0.095
10	0.38	0.41	0.175
15	0.90	0.96	0.45
20	1.45	1.55	0.77
25	2.03	2.16	1.10
30	2.55	2.70	1.45
40	3.55	3.85	2.15
50	4.1	—	—
60	5.1	5.5	3.2
70	6.0	6.4	4.1
80	7.1	7.3	5.0
90	7.65	7.9	5.55
100	8.2	8.5	6.2
110	8.6	8.7	6.7
120	9.0	9.2	7.2
283	16.9	(22.9)	12.15
350	13.6	13	13.1
400	14.0	13	13.9
500	14.0	13	14.5
600	14.0	—	14.4
700	16.0	—	16.1
800	16.0	—	18.4
900	15.0	—	17.7

[a] Data below 300 K are from capacitance dilatometer *in vacuo* and those above 300 K are from cycling in air in push-rod LVDT.

range together with earlier data for a YB18 [2] sample and MgO [13]. The results for BSC26 and BPSC8 above 300 K obtained by repeated cycling in air were reproducible after the first one or two cycles. However, in the case of BPSC6, the first heating gave large inflections in $\Delta l(T)$ near 300 and 700 K. On the next heating cycle, $\Delta l(T)$ increased almost linearly with T (corresponding to $\alpha \approx 13 \times 10^{-6}\,\mathrm{K}^{-1}$) until the sample fractured at 600 K.

4. DISCUSSION

Clearly there are difficulties in the BSC system due to mixture of 2212 and 2223 phases and latent instabilities which affect the reproducibility of thermal data. The average thermal expansion coefficient of bulk material at normal temperatures is not very different from that of YB and many common ceramic oxides. At low temperatures ($T < 30$ K) the coefficient is significantly larger for BSC reflecting the lower value of Debye temperature, namely, $\Theta_0 \sim 260$ K, compared with about 400 K for YB samples.

If our value of $\Delta\alpha \sim 0.2 \times 10^{-6}\,\mathrm{K}^{-1}$ near T_c is roughly correct, we may compare this with values of ΔC and the pressure dependence of T_c via the Ehrenfest relation:

$$\frac{1}{T_c}\frac{dT_c}{dP} = 3V\frac{\Delta\alpha}{\Delta C}$$

Schirber et al. [14] determined dT_c/dP for BSC samples as follows:

$$0.24 \pm 0.02\ \mathrm{K \cdot kbar^{-1}} \quad \text{for} \quad T_c = 85\ \mathrm{K}$$

$$0.16 \pm 0.05\ \mathrm{K \cdot kbar^{-1}} \quad \text{for} \quad T_c = 108\ \mathrm{K}$$

Using a molar volume of 180 cm^3 ($\rho \approx 5\ \mathrm{g \cdot cm^{-3}}$) and a mean value of 0.2 $\mathrm{K \cdot kbar^{-1}}$, we calculate $\Delta C \sim 5\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ or $\Delta C/T_c \approx 50\ \mathrm{mJ \cdot mol^{-1} \cdot K^{-2}}$. The review by Gmelin [15] quotes values from 0 to 24 $\mathrm{mJ \cdot mol^{-1} \cdot K^{-2}}$ from measurement of heat capacity. Clearly there is need for more thermal measurements on well-characterized samples.

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