Dilatometric study of new phase transitions in $YBa_2Cu_3O_{6.9}$

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We have observed dilatometrically two phase transitions in samples of $YBa_2Cu_3O_{7-x}$ with $x \sim 0.1$ prepared in three separate laboratories. These two transitions have been observed previously in heat-capacity measurements in $YBa_2Cu_3O_{6.9}$ in the range from about 87 to about 95 K. Recent heat-capacity measurements on one of the samples have also exhibited two transitions that correspond to the dilatometric results.

There have been several recent reports[1-3] in the literature of indications from specific-heat measurements of the existence of two phase transitions in the neighborhood of the superconducting transition in $YBa_2Cu_3O_{7-x}$ with $x = 0.1$. A recent comparison of the specific heat of superconducting and nonsuperconducting stoichiometries of this compound led to the conclusion "that there is indeed a second phase transition (martensitic transformation?) occurring near the superconducting transition in all these systems."[4]

To further clarify the nature of these transitions we have carried out measurements of the thermal expansion of polycrystalline samples of $YBa_2Cu_3O_{0.9}$ in the temperature range from 78 to 100 K using capacitance dilatometry.[5] Three sets of samples were examined. The first set of samples was cut from the same samples used in the specific-heat measurements in which phase transitions at about 87 and 91 K were observed,[1] the second set of samples was prepared by B. Fisher of Technion, and the third was prepared by B. Veal of Argonne National Laboratory. Sample preparation was by standard techniques, some details of which may be found in Refs. 1 and 2 and references therein. The temperature, measured with a calibrated silicon diode, was allowed to drift up at a rate of about 1 mK/sec and data were collected at intervals of about 1 sec using a microcomputer-based data acquisition system. Unfortunately, the system parameters did not allow measurements to be made on cooling, which would have given information on any hysteresis.

The results shown in Fig. 1 show the relative thermal expansion of the samples on warming. The measurements are relative to the brass dilatometer cell and a constant slope has been subtracted, so that absolute changes and slopes are meaningless, but relative changes in length and changes in the slope (changes in the thermal-expansion coefficient) are meaningful. For the sample prepared at the University of Pittsburgh small first-order length changes are observed at about 88.5 and about 93.4 K. The length change at 88.5 K is about $(3 \pm 1) \times 10^{-7}$ corresponding to a volume change of about 1×10^{-6}. The length change at 93 K is about $(3 \pm 1) \times 10^{-7}$, also corresponding to a volume change of about 1×10^{-6}. Data on the three samples are summarized in Table I. Similar anomalies were found in the samples prepared at Technion. In the sample prepared at Argonne National Laboratory, the higher-temperature first-order transition occurs at about 94.5 K and the lower transition appears to be truly of higher order, appearing as a barely detectable change in slope at about 90 K. Heat-capacity measurements presently underway at the University of Pittsburgh on a sample from the same batch as the sample prepared at Argonne National Laboratory have shown two transitions, a λ anomaly corresponding to a second-order transition occurring at 90.2 K and a break in the heat capacity corresponding to a first-order transition occurring at 94.5 K.

In addition, it should be noted that the temperatures at which the anomalies occur in the three sets of samples differ by several degrees. It is likely that such differences are due to small differences in oxygen concentration. It is

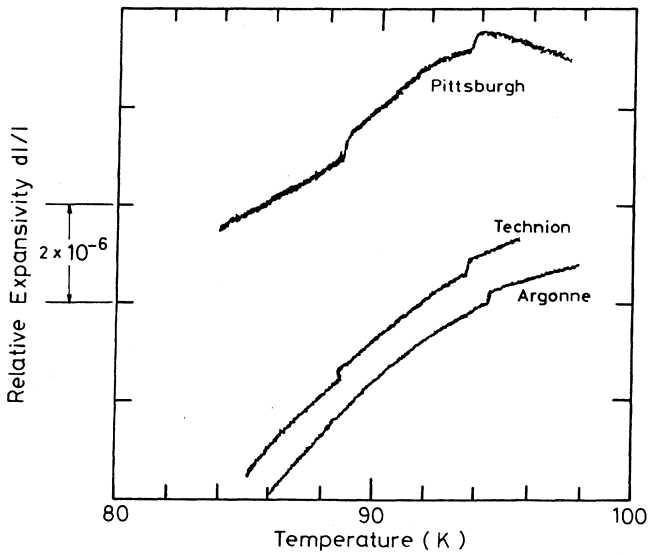

FIG. 1. Relative expansivity (dl/l) of the three samples relative to the brass dilatometer cell as a function of temperature on warming.

TABLE I. Data on three samples of $YBa_2Cu_3O_{6.9}$. Temperatures are ± 0.2 K and dl/l values are $\pm 1\times10^{-7}$.

Sample	Lower T (K)	$dl/l\times10^7$	Higher T (K)	$dl/l\times10^7$
University of Pittsburgh	88.6	3	93.5	3
Technion	88.7	2.5	93.6	2.5
Argonne National Laboratory	90.0	· · ·	94.5	2

interesting to note that the difference between the two transition temperatures is roughly the same for all three samples.

Previous dilatometric studies[6–11] have shown no effects suggestive of a first-order transition in the vicinity of the 90-K superconducting transitions (although there are suggestions in the work of Anshukova *et al.*[12] and Golovashkin *et al.*[13]), or in the vicinity of 36 K in La_2CuO_4.[9] Srinivasan *et al.*[14] have observed an anomalous variation in the c lattice parameter around 90 K and have shown very large hysteretic effects between warming and cooling runs in sound velocity measurements.

Use of the Clausius-Clapeyron equation allows one to obtain values of dT_c/dP for each first-order transition. We make the poor assumption of an isotropic distribution of orientations of grains in the samples, so that $dV/V = 3dl/l$. We use the area under the curves in Ref. 1 for the latent heat at the higher-temperature transition measured on a sample from the same batch. We then obtain $dT_c/dP = 2.5\times10^6\ dV/V$ K/GPa. Using the value of dl/l obtained at 93 K on the sample prepared at the University of Pittsburgh, we find $dT_c/dP = 2.5$ K/GPa. Lang *et al.*[9] have discussed the difficulty of direct measurements of this quantity and refer to other measurements of the specific heat in the neighborhood of T_c.

Recent ac-susceptibility measurements by Couach *et al.*[15] have been interpreted in terms of several superconducting transition temperatures characteristic of a succession of superconducting layers, due to spatial modulation of the oxygen intercalation. It is possible that we are seeing some indications of the same phenomenon here.

Duan, Lu, and Zhang[16] have suggested that $YBa_2Cu_3O_7$ may not be a bulk superconductor and state that "results are consistent with a picture where superconducting twin boundaries are formed in the bulk semiconducting matrix." If one notes this, together with the observation of Braun *et al.*[4] that the second transition is common to both the superconducting and nonsuperconducting phases, it becomes clear that detailed further studies will be required to determine the changes in the manifestations of the transitions as oxygen content is varied, before any clear understanding of their mechanism can be achieved. The obvious extension of this work to measurements on single crystals is in progress and will be pursued as larger crystals, suitable to dilatometric measurements, become available.

Recently Goldschmidt[17] has observed two transitions in $YBa_2Cu_3O_{7-d}$ in the temperature derivative of the resistance, and Wang *et al.*[18] have observed two transitions in the specific heat of $GdBa_2Cu_3O_{7-y}$. In both cases, the separation between the two transitions was about 4 K.

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