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Superconductivity and oxygen ordering in $(Ca,Ba,La)Cu_3O_{7-\delta}$

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Magnetization measurements on polycrystalline samples with nominal composition $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_{7-\delta}$ ($x=0.0$, 0.05, 0.10, 0.50, and 1.0) show that only samples with $x=1.0$ or 0.0 contain a single *superconducting* phase. Gas evolution experiments on $(Ca,Ba,La)Cu_3O_{7-\delta}$ ($x=1.0$, $\delta \sim 0.07$) reveal the presence of an oxygen phase that is indistinguishable from the oxygen chain structure of $YBa_2Cu_3O_{7-\delta}$ ($x=0.0$, $\delta \sim 0.05$); however, the total amount of evolved oxygen is very different between the two phases. These studies suggest that two phases coexist in $(Ca,Ba,La)Cu_3O_{7-\delta}$: a *superconducting* phase in which La^{3+} ions occupy the Y^{3+} sites, and a second *nonsuperconducting* phase where Ca^{2+} ions occupy the Y^{3+} sites.

INTRODUCTION

The compound $(Ca,Ba,La)Cu_3O_{7-\delta}$ is an interesting high-temperature superconductor that is expected to be electronically isomorphic to $YBa_2Cu_3O_{7-\delta}$, although it has a lower transition temperature, $T_c=80$ K. Early studies[1] suggested that the compound has the same structure as the tetragonal form of $YBa_2Cu_3O_{7-\delta}$. However, recent electron-diffraction studies[2-4] indicate a doubling of the unit cell along all crystallographic axes. A model has been proposed[2] to explain this phenomenon in which it has been suggested that substantial amounts of Ca^{2+} occupy the Y^{3+} sites and that the La^{3+} ions are distributed among the Ba^{2+} sites in a way that explains the supercell formation. In addition, the oxygen atoms that form the chains in $YBa_2Cu_3O_{7-\delta}$ are believed to cluster around the La^{3+} ions. In an effort to gain an understanding of how such a redistribution of the cation charges within the triple perovskite structure affect superconductivity, we have investigated a number of physical properties of the system with nominal composition $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_{7-\delta}$.

Since the possibility exists that a variety of oxygen phases are present, which could not be distinguished by structural studies, we have obtained additional information regarding the binding energy of the oxygen atoms by performing gas evolution and thermogravimetric experiments. In this fashion the oxygen evolved, as well as the oxygen remaining in the sample, were measured and cross checked with additional independent iodometric titration experiments. Superconducting properties were also determined using transport as well as magnetic measurements.

EXPERIMENTAL

Samples with the nominal composition $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_{7-\delta}$ ($x=0.0$, 0.05, 0.1, 0.50, and 1.0) were prepared by solid-state reaction of appropriate mixtures of high purity (99.99%) $CaCO_3$, $BaCO_3$, Y_2O_3, and CuO. The powders were first dried and outgassed and then mixed and ground in an agate mortar. Four firings of 24 h at 950 °C in air, each with intermediate grindings, were performed in alumina crucibles. Next, the powders were pressed into pellets and annealed in 1 atm of oxygen at 950 °C for 24 h, followed by slow cooling (~1 °C/min) to 400 °C where they remained for 24 h before a final slow cool to room temperature. For samples with $x=0.05$ and 0.1, x-ray diffraction patterns may be indexed according to the orthorhombic $YBa_2Cu_3O_{7-\delta}$ structure, whereas samples with $x=0.5$ and 1.0 correspond to the tetragonal form of $YBa_2Cu_3O_{7-\delta}$. The $x=1$ compound, $(Ca,Ba,La)Cu_3O_{7-\delta}$, has $\mathbf{a}=3.863$ Å and $c \sim 3\mathbf{a}=11.589$ Å. Peak intensities from other known phases, in particular CuO, CaO, and Ca_2CuO_3, never exceeded 4% of the main diffraction peak intensity. Rietveld refinement of neutron-diffraction data for the $x=1$ compound obtained at Argonne National Laboratory[5] did not converge toward a structure isomorphic to the tetragonal form of $YBa_2Cu_3O_{7-\delta}$. Samples with $x=1$ were prepared three times under slightly different firing and annealing conditions without significant changes in the structural or physical properties. Oxygen-deficient samples were obtained by (i) equilibrating the specimens at various temperatures in air, He, or Ar atmospheres, followed by slow cooling or quenching to room temperature, and (ii) by heating the specimens in closed, evacuated tubes with a Zr getter foil.[6] Oxygen contents were determined by iodometric titration,[7] assuming that the valences in the presence of excess I^- in acidic solution are 1+, 2+, 3+, and −2 for Cu, (Ba,Ca), (Y,La), and O, respectively. Electrical resistivity and magnetoresistance measurements were performed on bar shaped specimens by a standard four probe technique.[8] dc magnetic susceptibility measurements were made in fields of 2.5×10^{-4} T using a SHE model VTS-50 SQUID magnetometer. The radio frequency (32 MHz) magnetic susceptibility was measured by observing the resonant frequency F of an oscillating circuit as a function of temperature.[9] A Cahn RG 2000 electrobalance was used for thermogravimetric analysis, in which samples were dried at 120 °C prior to analysis. Oxygen evolution was measured[10] by placing the sample in a closed quartz tube and measuring the pressure and temperature as the sample was heated at a constant rate of 10 °C/min from room temperature to 900 °C. The composition of the gases evolved was analyzed using mass spectrometry. When exposed to air for long periods, (Ca,Ba,La)$Cu_3O_{6.93}$ was found to take up considerable amounts of CO_2.

RESULTS

Figure 1 shows a comparison of the temperature derivative of the rf magnetic susceptibility signal F normalized to the mass m of the sample, as a function of temperature T. The curves are shifted along the y axis for clarity. A peak corresponds to a superconducting transition, and it is clearly evident that T_c is depressed with increasing x (curves a–d). For $x=0.1$ and 0.5, however, two distinct peaks are observed, indicating that samples with these nominal compositions have separated into two superconducting phases. Samples with $x=1$ again contain a single superconducting phase as shown by curves e and f, which correspond to different annealing conditions of the same sample. First the sample was heated to 950 °C in vacuum followed by slow cooling at a rate of 10 °C min to room temperature in 1 atm of oxygen (curve e). After measuring the susceptibility the sample was again heated to 950 °C and slow cooled in oxygen to 400 °C, where it was kept for 24 h before the final slow cool to room temperature (curve f). The different treatments do not affect T_c. However, the rf susceptibility, proportional to the area under the $m^{-1}(dF/dT)$ curves, increased by $\simeq 10\%$ as a result of the prolonged annealing at 400 °C. Since samples with $x=0.1$ and 0.5 are multiphase, we assume that phase separation characterizes all samples with intermediate substitutions ($0.1 < x < 1.0$) and discuss in the following only compounds consisting of a single superconducting phase, namely those with $x=0$ or $x=1$.

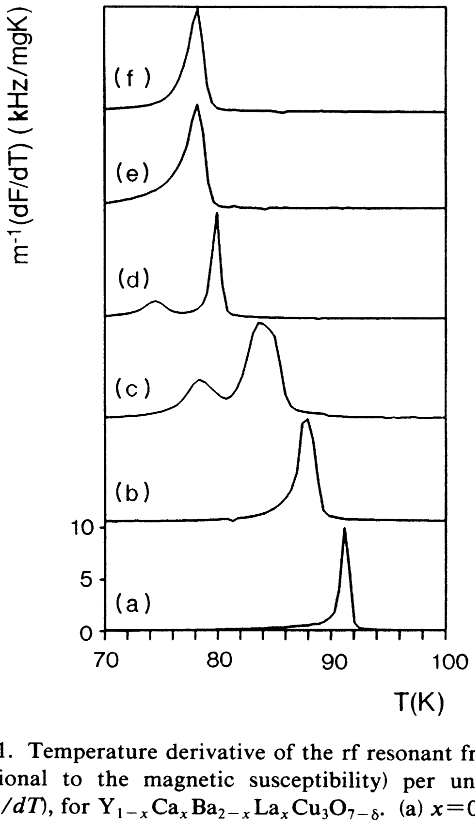

FIG. 1. Temperature derivative of the rf resonant frequency (proportional to the magnetic susceptibility) per unit mass, $m^{-1}(dF/dT)$, for $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_{7-\delta}$. (a) $x=0.0$ (×1), (b) $x=0.05$ (×5), (c) $x=0.10$ (×13), (d) $x=0.50$ (×4), (e) $x=1.0$ (×3), (f) $x=1.0$ (×2).

Evidence of bulk superconductivity was obtained from dc magnetic susceptibility measurements on (Ca,Ba,La)$Cu_3O_{6.93}$. Zero-field-cooling and field-cooling curves, respectively, show a 70% diamagnetic shielding signal and a 25% Meissner signal in a field of 2.5×10^{-4} T. The onset of the diamagnetic signal occurs at $T=80$ K, in agreement with rf susceptibility measurements. The resistive transition of (Ca,Ba,La)$Cu_3O_{6.93}$, shown in Fig. 2, also corroborates the $m^{-1}(dF/dT)$ data of Fig. 1 (curves e and f). A sharp drop in resistivity from 90% to 10% of its normal-state value is observed over a temperature range of 1.6 K. The 50% drop occurs at 80.6 K, defined here as the transition temperature, which agrees well with the temperature (79 K) at which the peak of $m^{-1}(dF/dT)$ occurs.

Upper critical field, H_{c2}, measurements for (Ca,Ba,La)$Cu_3O_{6.93}$ are displayed in Fig. 3. At low fields ($H < 6$ T), a slight curvature of the H_{c2} versus T curve is observed, which seems to be characteristic of ceramic samples[8] and which was shown to be present in conventional inhomogeneous superconductors.[11] At higher fields ($H \geq 6$ T), a linear dependence of H_{c2} on T is found, and we estimate the upper critical field slope for the transition midpoint, dH_{c2}/dT, to be ~ -2.7 T/K (Fig. 3, solid squares). We note that this slope has been suggested to reflect flux lattice melting phenomena rather than the Ginzburg-Landau coherence length for the supercon-

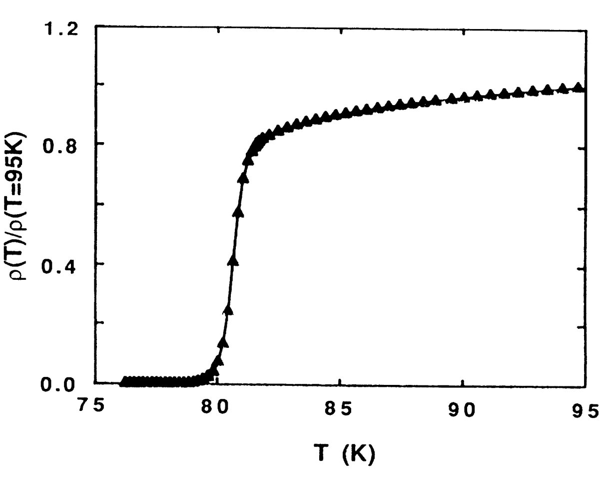

FIG. 2. Normalized resistivity $\rho(T)/\rho(T=295\text{ K})$ vs temperature for (Ca,Ba,La)$Cu_3O_{6.93}$.

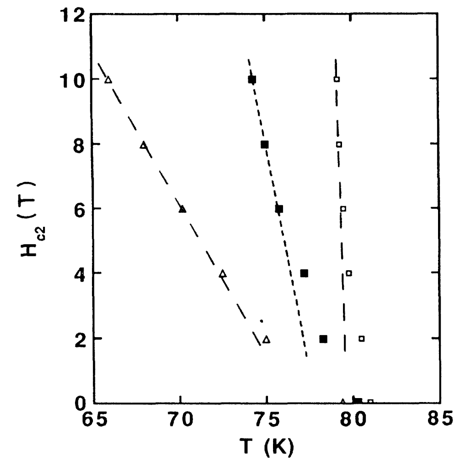

FIG. 3. Upper critical field H_{c2} vs temperature T curves for $(Ca,Ba,La)Cu_3O_{6.93}$. Triangles, solid squares, and open squares indicate 10%, 50%, and 90% of the normal-state resistivity, respectively.

ducting state.[12] The value of the upper critical field slope for $(Ca,Ba,La)Cu_3O_{6.93}$ is comparable to the values[8,13] found for ceramic $YBa_2Cu_3O_7$. This, together with the broadening of the transitions, indicates that superconductivity in both compounds is of a similar nature. Assuming that dH_{c2}/dT measured resistively reflects the superconducting coherence length ξ, we estimate $\xi \approx 12$ Å by using the standard, three-dimensional, type-II, dirty-limit theory.[14]

Thermogravimetric analysis of $(Ca,Ba,La)Cu_3O_{6.93}$ in air, which measures the oxygen content of the sample, is displayed in Fig. 4. Above 400 °C, oxygen is continuously lost and at ~925 °C the oxygen content is ~6.55. Note that this concentration is obtained by normalizing to the *total* weight of the sample. In a similar experiment,[15] $YBa_2Cu_3O_{6.9}$ loses oxygen until $(7-\delta)$ ~6.1. Above 925 °C, a rapid decrease in the oxygen content for $(Ca,Ba,La)Cu_3O_{7-\delta}$ is observed, indicating that a new decomposition channel has opened up. Upon cooling, a similar curve is followed which corresponds to an uptake of slightly less oxygen than the amount released by heating. This should be expected since the sample was initially annealed in a pure oxygen atmosphere. Cycling at higher partial pressures of oxygen closes the gap between the cooling and heating curves.[3]

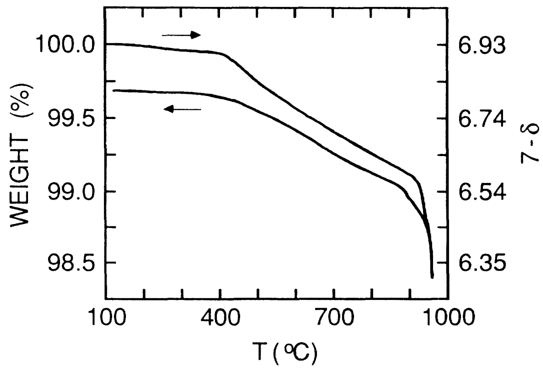

FIG. 4. Weight loss of $(Ca,Ba,La)Cu_3O_{6.93}$ measured thermogravimetrically at a heating and cooling rate of 7 °C/min in air. The right y axis shows the oxygen content of the sample calculated from the weight loss.

In order to estimate the thermal activation energy of the loosely bound oxygen, and to identify the composition of the gases leaving the samples, we have performed a series of desorption experiments.[10] The desorption peaks for $(Ca,Ba,La)Cu_3O_{7-\delta}$ can be fitted to a simple theory describing first-order desorption from a single site:

$$d\delta/dt=\mu(\delta_0-\delta)\exp(-\Delta G/k_BT) ,$$

where μ is a frequency factor, δ_0 and δ represent the concentrations of initial and evolved oxygen, and ΔG is a free-energy barrier for activation.[10] Figure 5 shows the desorption data for $(Ca,Ba,La)Cu_3O_{7-\delta}$ (curve *a*) together with desorption data for $YBa_2Cu_3O_{7-\delta}$ (curve *b*) for comparison. It is clear that the desorption peak for both samples is centered around the same temperature (~480 °C), and this is reflected in the fit to the single-site activation energy which for both samples yields $\Delta G=1.36$ eV and $\mu=5\times10^7$ Hz. The difference in the peak heights shows that roughly half as much oxygen is evolved from $(Ca,Ba,La)Cu_3O_{7-\delta}$ as for $YBa_2Cu_3O_{7-\delta}$ ($\delta\sim0.05$), and this agrees with the results from the thermogravimetric analysis.

The transition temperature T_c versus oxygen concentration $(7-\delta)$ for $(Ca,Ba,La)Cu_3O_{7-\delta}$ is displayed in Fig. 6(a). Transition temperatures were measured resistively and the vertical bars represent the transition width. Horizontal bars indicate the uncertainty in the determination of the oxygen content by chemical titration. Triangles show T_c's of specimens derived from oxygen-annealed samples by heating them to various temperatures in air, He, or Ar followed by slow cooling (solid) or quenching (open). This treatment immediately leads to broader transitions and a sharp drop in T_c to ~68 K when $(7-\delta)$ is decreased from ~6.93, which is the value of the

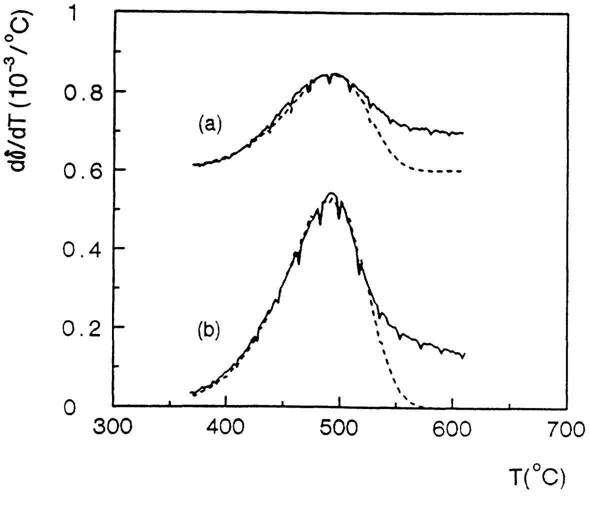

FIG. 5. Oxygen desorption curves of (a) $(Ca,Ba,La)Cu_3O_{7-\delta}$ ($\delta\approx0.07$) and (b) $YBa_2Cu_3O_{7-\delta}$ ($\delta\approx0.05$), together with theoretical fits (dashed curves) for single-site desorption.

oxygen-annealed samples, to ~6.85. Further oxygen depletion apparently leads to an increase in T_c which reaches a local maximum at ~78 K when $(7-\delta)\sim 6.81$. Beyond this point superconductivity is rapidly quenched and disappears at $(7-\delta)\sim 6.7$. Samples represented by solid squares were prepared with a Zr getter technique and these yield the same trend. Taken at face value, the T_c versus $(7-\delta)$ dependence for (Ca,Ba,La)$Cu_3O_{7-\delta}$ appears to be completely different from $YBa_2Cu_3O_{7-\delta}$. This point will be addressed in the following.

X-ray diffraction measurements of the oxygen-depleted samples reveal broadened or split diffraction lines for samples with $(7-\delta)<6.8$, indicating that the rapid drop of T_c beyond this oxygen stoichiometry is accompanied by structural changes. In particular, quenched samples, represented by open triangles, showed a splitting of the $[hkl]=[200]$ and [006] peak resulting from an expansion of the c axis by up to 0.14 Å and, consequently, a departure from a pseudocubic structure. A similar behavior has been reported by Cava *et al.*[16] for the $YBa_2Cu_3O_{7-\delta}$ system and occurs at $(7-\delta)\sim 6.3$.

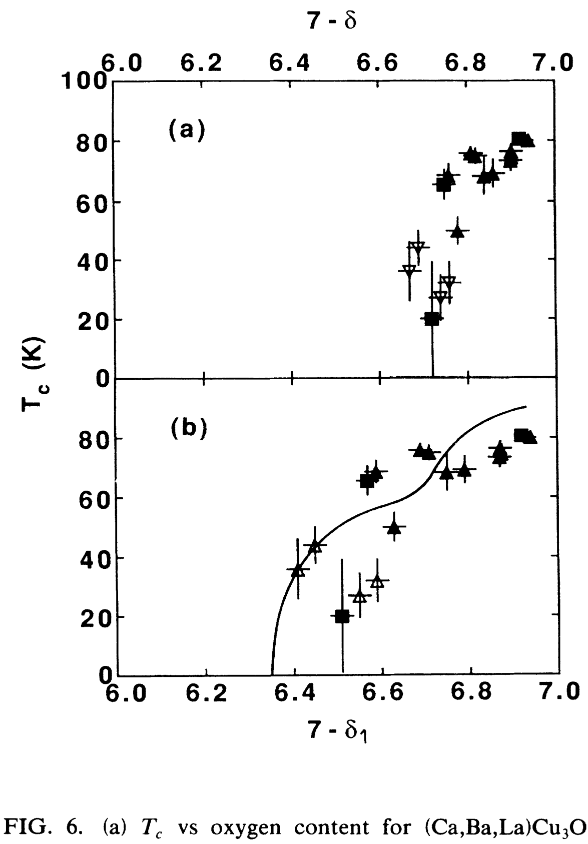

FIG. 6. (a) T_c vs oxygen content for (Ca,Ba,La)$Cu_3O_{7-\delta}$. Vertical bars represent the resistively measured transition width (10–90% drop of the normal-state value), and horizontal bars the uncertainty in oxygen content. Triangles: samples heated to various temperatures in air, He, or Ar followed by slow cooling (solid) or quenching (open). Solid squares: samples prepared by the Zr getter technique. (b) T_c vs oxygen content for (Ca,Ba,La)$Cu_3O_{7-\delta}$ renormalized according to the assumption that oxygen is evolved only from the La(Ba,Ca)$Cu_3O_{7-\delta_1}$ phase which accounts for ≈50% of the multiphase (Ca,Ba,La)$Cu_3O_{7-\delta}$. The solid line indicates the trend of the $YBa_2Cu_3O_{7-\delta}$ data.

DISCUSSION

The gas evolution experiments show that the binding energy of the loosely bound oxygen ions in (Ca,Ba,La)$Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ are the same within the experimental error. This behavior would not be expected if (Ca,Ba,La)$Cu_3O_{7-\delta}$ is characterized by an oxygen phase completely different from the chain structure found in $YBa_2Cu_3O_{7-\delta}$.[2] If an ordered phase, in which the O(1) atoms cluster around the La^{3+} ions ordered at the Ba^{2+} sites,[2] is a correct description of the (Ca,Ba,La)$Cu_3O_{7-\delta}$ structure, then the following assumptions must be made: (1) the binding energies of these clusters match exactly the binding energy of the O(1)'s in $YBa_2Cu_3O_{7-\delta}$, and (2) the equivalent sites in the oxygen clusters become inequivalent upon oxygen depletion in a way that leaves $\sim\frac{1}{2}$ of the oxygen ions strongly bound. However unlikely, this possibility cannot be completely excluded by the present experiment.

A more natural explanation of the desorption data, which also explains the thermogravimetric measurements, involves the assumption that ~50% of the sample has O(1) ordering very similar to $YBa_2Cu_3O_{7-\delta}$. Since clusters are unlikely to be found around La^{3+} ions at the Ba^{2+} sites, this phase should have all La^{3+} ions at the Y^{3+} sites and the Ca^{2+} ions distributed among the Ba^{2+} sites, which makes the charge distribution in the crystal identical to that of $YBa_2Cu_3O_{7-\delta}$. In the following, this phase is referred to as La(Ba,Ca)$Cu_3O_{7-\delta_1}$. The remaining phase could be characterized by La^{3+} ions at the Ba^{2+} sites [Ca(Ba,La)$Cu_3O_{7-\delta_2}$] leading to strongly bound O(1) clusters which do not contribute to the desorption peak observed at 480 °C. This second phase may be the one observed by electron diffraction.[2-4] We note that the desorption experiments are microscopic in nature, i.e., even a phase separation which extends only over a few lattice parameters may be in accordance with the experimental results. A purely random distribution of Ca and La ions at the Y site would lead to an ~1:1 ratio of the two phases, assuming that Ba has no affinity for the Y sites. This is in rough agreement with the thermogravimetric measurement where it is observed that only $\sim\frac{1}{2}$ as much oxygen is lost between 450 and 925 °C as for $YBa_2Cu_3O_{7-\delta}$.

Since the desorption and thermogravimetric data indicate the presence of two phases of which only one loses oxygen between 420 and 925 °C, we have tried to replot the T_c versus $(7-\delta)$ data of Fig. 6(a) according to the assumption that oxygen is lost *only* from the La(Ba,Ca)$Cu_3O_{7-\delta_1}$ phase. The replotted data are displayed in Fig. 6(b) where the x axis has been renormalized according to the equation

$$(7-\delta)=\tfrac{1}{2}[(7-\delta_1)+(7-\delta_2)]\ ,$$

where the prefactor of $\frac{1}{2}$ comes from the assumed 1:1 ratio of the two phases. Since the oxygen vacancy concentration after oxygen annealing of the mixed-phase sample is close to that of single-phase $YBa_2Cu_3O_{7-\delta}$ ($\delta\approx 0.05-0.07$), we choose the initial value of $\delta_1=\delta_2=0.07$. Also shown in Fig. 6(b) is the trend of the data for $YBa_2Cu_3O_{7-\delta}$, which, except for the plateau, is similar to the T_c versus $(7-\delta_1)$ data. It is not surprising that the two T_c versus $(7-\delta)$ curves do not match exactly, taking into account the complicated two phase nature of the $(Ca,Ba,La)Cu_3O_{7-\delta}$ system. Since this picture indicates that superconductivity in the entire sample may be quenched by oxygen depleting the $La(Ba,Ca)Cu_3O_{7-\delta_1}$ phase only, the second phase, presumably $Ca(Ba,La)Cu_3O_{7-\delta_2}$, cannot be a high-temperature superconductor, as first anticipated.

We conclude that ceramic samples with nominal composition $(Ca,Ba,La)Cu_3O_{7-\delta}$ are most likely to be multiphase. Roughly half the sample consists of a superconducting phase and the remaining phase(s) is (are) nonsuperconducting. None of the standard measures of bulk superconductivity show this phase separation, and it is not clearly visible in the standard diffraction measurements, indicating the intimate and complicated nature of the phase diagram of samples with nominal composition $(Ca,Ba,La)Cu_3O_{7-\delta}$.

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