Variation of T_c and resistivity in charge-compensated $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$

D. Goldschmidt, A. Knizhnik, Y. Direktovitch, G.M. Reisner, and Y. Eckstein

Department of Physics and Crown Center for Superconductivity, Technion Israel Institute of Technology, Haifa 32000, Israel

(Received 2 November 1993; revised manuscript received 25 January 1994)

We report careful measurements of the transition temperature T_c of (Ca_xLa_{1-x}) $(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ as a function of oxygen content y, mainly for compositions $x = 0.1$ and 0.4. This 1:2:3 superconductor family, that exists in the composition range $0 \leq x \leq \sim 0.5$, is tetragonal and has a maximal T_c of ~ 82 K. Through mutual charge-compensating cosubstitutions, it preserves a constant charge on the noncopper cations ($Q = 7.25$), independent of x. We observed a monotonic decrease in T_c as y varies from the initial value ~ 7.15 to the insulator state roughly at $y \simeq 6.9$. At the metal-insulator (MI) transition, the value of y_{MI} decreases with increasing x. Most unusual is the substantial increase in T_c by 21–24 K when x changes from 0.1 to 0.4, under conditions where the charge density remains constant. It is accompanied by a twofold decrease in resistivity ρ. We attribute this to the change in band structure with composition x, which occurs due to increase in Ca content and to oxygen redistribution near La that substitutes for Ba. This induces a net electron transfer from the planes to the disordered chains. This assumption is supported by the decrease in y_{MI} and in lattice parameters with increasing x. It implies that changes in mobile hole density, which are responsible for the increase in T_c and decrease in ρ, take place despite the total charge density being constant.

I. INTRODUCTION

Recently we have investigated the new family $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$, which belongs to the 1:2:3 system.[1] It is tetragonal ($P4/mmm$ symmetry) throughout its range of existence $0 \leq x \leq \sim 0.5$. Ca occupies the Y site in concentrations not exceeding $x = 0.5$, while La (totaling 1.25 per formula unit) shares both the Y and Ba sites [we use the site notation of $YBa_2Cu_3O_y$ (YBCO)]. In accordance with other investigations,[2] we observed that the $x = 0.5$ member of this family is the actual material obtained when attempting to prepare the so called "$CaLaBaCu_3O_y$" material. Meanwhile there have been electron microscopy[3] and neutron diffraction[4] studies on closely related families, confirming our observations. In particular, all diffraction methods agree about the tetragonal structure, the maximum Ca content, and the site occupancy of Ca. The tetragonal structure does not rule out the possibility of short-range nontetragonal distortions, unresolvable by diffraction methods. In this case one might expect microtwinning to occur within a short length scale.

Our interest in this family was the possibility of investigating effects of charge compensation due to equal amounts of substitution on the Y and Ba sites. Hence, Q (the total formal valence of the noncopper cations) is constant independent of x (i.e., $Q = 7.25$; see Sec. IV). When the oxygen content y is maintained constant this family becomes isoelectronic, that is, the chemically determined total hole density is independent of x. As the mobile and chemical hole densities are believed to be related to one another, T_c was expected to remain constant, independent of x. Instead, T_c varied from ~ 45

K at $x = 0$ to ~ 80 K at $x = 0.4$.[1] In reality though, y did not remain strictly constant, but increased by ~ 0.1 over the range $x = 0$ to $x = 0.4$. In an attempt to hold y strictly constant we have reduced the oxygen content in the high-x members of this family. We extracted from these preliminary data a change of ≈ 30 K in T_c at constant y and Q (i.e., with changing x) suggesting that a big change in T_c takes place at apparently constant hole density. This indicates that modifications in the estimates of hole density or in the relationships between T_c and hole density (e.g., the parabolic relationship) might be required.

After publication we realized that some of the reduced samples might be inhomogenous in oxygen distribution. Such inhomogeneities would artificially shift T_c, exhibiting an erroneous plateau of T_c vs y, together with an extremely sharp transition into the insulating state. Therefore, we performed new reduction experiments on this family.

In this paper we report careful and systematic oxygen reduction experiments. Macroscopic oxygen homogeneity has been achieved through high annealing temperatures and confirmed by the low transition width. The new results differ somewhat from the previous ones,[1] owing to the better homogeneity. Nevertheless they confirm the major conclusions obtained previously. These were the following.

(1) T_c varies (by 21–24 K) when the chemically determined mobile hole density remains constant.

(2) Unlike in YBCO, the transition from the region of maximal T_c to the nonsuperconducting ("insulator") state takes place within a narrow range of oxygen content, i.e., from $y \cong 7.15$ to $y \cong 6.9$.

(3) A dramatic semiconductorlike behavior of the resistivity $\rho(T)$ appears with only a small decrease in y even in samples that undergo a superconducting transition.

II. EXPERIMENTAL

Sample preparation by solid-state reaction has been described elsewhere.[1] Essentially, raw powders were machine mixed under N_2 atmosphere fired in air at 950 °C for one day, removed from the hot furnace and reground; this sequence was repeated three times. Formation of small crystallites during the firing step acts in favor of narrow transitions, low resistivities, and increased hardness of the samples. This could be assisted by adding to the third firing small amounts of powder left over from the first firing. After pelletizing, samples were sintered for 70 h in flowing oxygen at 970 °C and cooled at a rate of 10 °C/h to room temperature. "As-prepared" samples (i.e., after sintering and before reduction) had high oxygen content (y changing between 7.05 and 7.15, depending on x), and were phase pure. In the final batch of samples (no. 6) we attempted to further increase the oxygen content via a multistep cooling process consisting, in addition, of six one-day soaks at temperatures 400, 350, 320, 300, 280, and 260 °C. This increased y only slightly and had no other apparent effect on physical properties, implying that as-prepared samples approach the limit of oxygen solubility in these materials.

The oxygen reduction was carried out in a tube furnace using either flowing N_2 gas containing 50 (or Ar with 25) ppm of O_2, or pure O_2. For N_2, the samples were kept for 16 h at an annealing temperature in the range of 300–430 °C, and then removed from the furnace or cooled at a rate of 15 °C/h to room temperature. For small reduction in the oxygen content, which required low annealing temperatures, signs of inhomogeneity have been observed such as the appearance of an additional peak in the imaginary part of the susceptibility χ''. This inhomogeneity could severely affect our results by creating an artificial plateau in the dependence of T_c on y. Therefore, we performed most reductions in pure O_2, which allowed annealing at temperatures 100–200 °C higher than in N_2, followed by quench into liquid nitrogen, thereby improving oxygen homogeneity. No aging effects on T_c were observed following this quench. The annealing curves of two compositions for both N_2 and O_2 atmospheres are shown in Fig. 1. Generally speaking, the O_2-quenched samples had a $T_c(y)$ dependence similar to the N_2 annealed samples, but the magnetic transition became half as wide, indicating better homogeneity.

The phase purity of our samples was checked by careful x-ray diffraction (XRD) measurements (Siemens D5000 powder diffractometer, Cu $K\alpha$ radiation) on both as-prepared and reduced samples in the range $10° \le 2\theta \le 140°$ using stepscan (0.02° step size, 8 sec per step). The intensity of the strongest line was on the order of several thousand counts, rendering the observation of impurity phases relatively easy.[1,2]

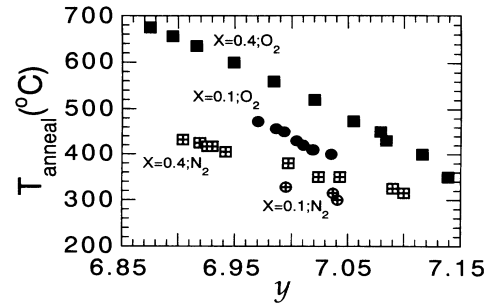Oxygen content was determined by iodometric titration[5] performed on a small fraction (typically < 10

FIG. 1. Oxygen content y as function of annealing temperature for O_2 and N_2 gas at atmospheric pressure. Notice that the $x = 0.1$ samples can be reduced at lower temperatures than the $x = 0.4$ samples.

mg) of the same sample on which we measured resistivity and susceptibility. The reproducibility of our measurements for a given sample was better than $\Delta y = \pm 0.005$. [In many cases, repetitions of titration B (Ref. 5) yielded a difference in the value of y as small as 0.002.] This value (0.005) also corresponds to the absolute accuracy between samples provided that small amounts of impurity phases, undetectable even under our high intensity XRD measurements, do not exist, or at least do not vary significantly from sample to sample. In fact, for the absolute error in y to be 0.01, the concentration of these hypothetical impurity phases should not exceed 2% (molar).[5] We note that the high accuracy in the determination of oxygen content and the small mass employed provided a direct and independent check of macroscopic homogeneity. For instance, we selected two samples (a good sample and a sample with two peaks in χ''), split them into three pieces each, and measured y on each piece separately. The difference in the values of y obtained in this way was twice as large in the sample exhibiting a double peak in χ'' as in the good sample. In an attempt to further check for possible inhomogeneity, we prepared thin (0.1 mm thick) disks that were processed together with the larger samples. The difference in oxygen content between the thin and thick pellets did not exceed the stated accuracy.

Additional indications that the O_2-annealed samples are close to equilibrium come from the reproducibility of our results at different thermal cycling. For instance, we compared y in two samples that were annealed at 400 °C. One was heated directly from room temperature, while the heating cycle of the second sample included a preheating step of 6 h at 600 °C. Similarly, we compared y in the usual heating schedule (16 h at 420 °C) to that in a longer anneal (48 h at 420 °C). In both tests the values of y did not differ by more than 0.002 from one sample to another.

Resistivity was measured by standard four-probe dc methods on samples pressed to a bar shape measuring $2.5 \times 2.5 \times 13$ mm^3 and containing gold-wire implanted contacts. The measurement current was usually 10 mA but currents ranging between 1 and 100 mA were occasionally employed in order to check the quality of the

grain boundaries.[6] ac magnetic susceptibility was measured at $\sim$ 1 kHz and at an estimated driving field of $\sim$ 25 mOe on small ($\sim$ 10–50 mg) samples cut across the bar. Temperature was measured with a calibrated Si diode, attached to the sample with Apiezon grease.

In this family, oxygen homogeneity is a crucial parameter that affects the quality of the results. In the course of our measurements, we examined more than 50 samples of the $x = 0.4$ and 30 of the $x = 0.1$ compositions, which were prepared in several batches. Most of them followed a definite and reproducible pattern in the dependence of T_c on oxygen content. Scatter in our data, which we observed in our early data points, correlates with inhomogeneous oxygen distribution, as the corresponding samples were reduced at low annealing temperatures. Scatter in the T_c vs y data is a result of the way these parameters are determined. T_c represents the superconducting portions of the sample having the highest oxygen content, while y represents an average over the entire sample. Thus, the measurements of T_c and of y weigh differently various parts of the sample. For instance, a broad distribution of oxygen content would result in an artificially higher T_c than in a uniform distribution; besides, the transition becomes wider. Therefore, we discarded some samples from our final set of data points, according to the following three criteria that are related to the width of the transition:

(a) ΔT_c (the transition width) at a given y is more than $1\frac{1}{2}$ times larger than the lowest value that we obtained (e.g., by the O_2 annealing and quench).

(b) The appearance of two peaks in χ'' becomes visible.

(c) $T_{c,0}^R$ (zero resistance at low measurement current) and T_c^χ (susceptibility onset) become widely separated, i.e., $T_{c,0}^R - T_c^\chi \geq 3$ K or $T_c^\chi - T_{c,0}^R \geq 1$ K.

This selection left more than 70% of the samples with $x = 0.4$ and more than 50% with $x = 0.1$ as representatives of the final good data points. In the curve representing T_c vs y, this selection removed most data points that fell off the curve as well as some data points that fell on the curve. For further details, see Sec. III.

Before reduction, it is essential to avoid contamination of the samples by reducing agents such as Apiezon grease. Samples that got contaminated by grease (e.g., during measurement at low temperatures) became, upon successive annealing, reduced in an uncontrolled manner, thereby yielding nontypical results. As mentioned in the Introduction, the reduced samples of our preliminary study[1] were prepared in this uncontrolled manner. This is the reason for the change in the T_c vs y curve of reduced samples between the present and our previous work.[1] The results described in this work correspond only to the controlled reduction procedures, as outlined in previous paragraphs, and do not include samples that had previously been subjected to contact with grease.

III. RESULTS

Our diffraction results for the $x = 0.1$ and $x = 0.4$ members of the family

$$(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$$
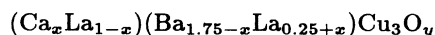
are summarized in Fig. 2. Figure 2(a) presents typical XRD spectra of the reduced samples. The reduced samples, as well as the more oxidized samples[1] (not shown), were all phase pure with no traces of impurity phases. All the lines could be indexed according to the tetragonal space group $P4/mmm$; no lines remained unidentified. The XRD spectra were, in fact, almost identical to those that we reported previously,[1] i.e., the more oxidized samples were approximately pseudocubic ($\frac{c}{3} \cong a$). The only observable difference in the reduced samples was an increase in the c axis so that, for instance, splitting of the (200) and (006) lines could be observed [see inset, Fig. 2(a)].

Lattice parameters as function of oxygen content are shown in Fig. 2(b). The trend, well known from other 1:2:3 compounds, that c increases with decreasing y is observed also in the present family; a, though, remains almost constant, as is typical of the average $\left(\frac{a+b}{2}\right)$ of the a and b axes in the orthorhombic structure. Interestingly, at any given y both lattice parameters of the $x = 0.1$ material exceed those of the $x = 0.4$ material. This confirms the trend we observed previously in the more oxidized samples,[1] that the lattice parameters decrease with increasing x. Moreover, this emphasizes that the changes in lattice parameters as function of composition
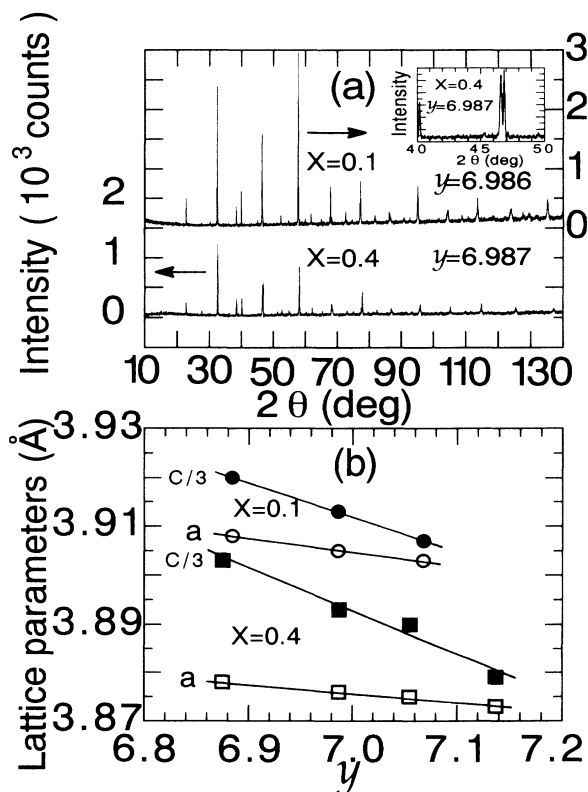

FIG. 2. (a) Typical x-ray powder diffraction pattern of reduced samples. Inset shows the splitting of the (200) and (006) lines. (b) Lattice parameters as function of oxygen content y, for samples reduced in oxygen. Lines are guides for the eye.

occur *even at constant y*. This observation suggests that changes in electron charge distribution take place when all parameters but x remain unchanged, i.e., under conditions where the total charge within a unit cell remains constant.

Our results of the onset resistive (T_c^R) and magnetic (T_c^χ) transition temperatures vs oxygen content for the $x = 0.1$ and $x = 0.4$ samples are shown in Figs. 3(a) and 3(b). There is a monotonic decrease in T_c from the highest T_c at $y \cong 7.15$ to the insulator state roughly at $y \cong 6.9$. In other words, there is no plateau in the dependence of T_c on y as seen in YBCO. Also unlike YBCO, the range in oxygen content from full to complete disappearance of superconductivity is quite narrow, i.e., $\Delta y \cong 0.25$. This implies that the metal-insulator (MI) transition has shifted to high oxygen content, that is, it occurs close to $y \cong 6.9$ as compared with $y \cong 6.4$ in YBCO. Notice that this transition falls at still higher oxygen content in the lower-x compositions.

In Figs. 3(a) and 3(b) one can see that, at constant oxygen content, T_c increases markedly when the cation composition varies from $x = 0.1$ to $x = 0.4$. This behavior was observed in both the resistivity and susceptibility measurements. For instance, for $y = 7.05$, T_c^R varies from ~ 42 K at $x = 0.1$ to ~ 63 K at $x = 0.4$, while T_c^χ varies from ~ 35 K to ~ 56 K. At $y = 7.00$, the difference in T_c increases from ~ 21 to ~ 24 K. As was noted in the Introduction, this large increase in T_c occurs at
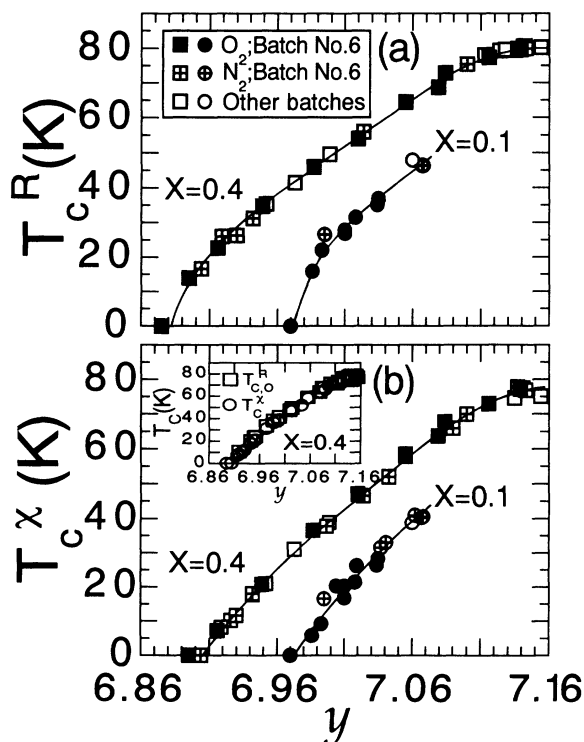

FIG. 3. Dependence of (a) the resistive-onset T_c^R and (b) the magnetic-onset T_c^χ transition temperature on oxygen content y. Curves are guides for the eye. Inset shows the coalescence of the zero-resistive $T_{c,0}^R$ and magnetic-onset transition temperatures.

apparently constant mobile hole density. This signals an unusual behavior within the cuprate superconductors, as discussed in the next section.

In our measurements we observed that $T_{c,0}^R$ (the temperature at which the resistance becomes first zero at small measurement current) coincides to within ~ 2 K with T_c^χ [i.e., $T_{c,0}^R \geq T_c^\chi$; see inset, Fig. 3(b)]. In the O_2-quenched $x = 0.4$ samples the agreement between these temperatures was better than 0.5 K in all but the lowest-y samples, implying that it is related to oxygen homogeneity. Similar coincidence of these temperatures has been observed in high quality single crystals of YBCO.[7] Apparently this reflects on the connectivity of the superconducting system, and seems to indicate good homogeneity of the samples: Zero resistance first appears when long superconducting paths percolate between grains and grain boundaries (or other weak links). Magnetic susceptibility onset occurs when large-area shielding loops, traversing many weak links, form. When the long superconducting paths form simultaneously with large-area shielding loops, these transition temperatures coincide. This happens when the weak-link intergranular network undergoes a superconducting transition throughout the entire sample at the same temperature (as would be characteristic of material with good homogeneity of oxygen distribution), thereby forming the weak links between already superconducting grains.

In order to further establish the relationship between magnetic susceptibility and the connectivity of the grain-boundary network, we split one of our disk-shaped samples into 20 pieces, keeping the total mass as well as the overall shape of the assembled sample unchanged. We observed a marked decrease in the mass susceptibility, i.e., χ'' decreased by a factor of ~ 4 (χ' decreased by a factor of ~ 3) by this splitting. This implies that before splitting, a large fraction of the susceptibility is associated with large loops that are much larger than the average size of a fragment ($\sim \frac{1}{2}$ mm) which, in turn, contains many grains.

In Fig. 4 we show the resistive (ΔT_c^R) and magnetic (ΔT_c^χ) transition widths. (We obtained ΔT_c by taking the derivative of $R(T)$ and of $\chi'(T)$. On these derivative curves we defined ΔT_c as the width at 40% of the maximum height [see inset in Fig. 4(a)]. This correlates well with the full width of the steep portion of the transition and avoids complications in the determination of ΔT_c, due to the tail related with grain boundaries.[6]) Our results of ΔT_c compare favorably with some of the best results of reduced ceramic YBCO (e.g., Refs. 8, 9), at least for $x = 0.4$. For instance, in the vicinity of the metal-insulator boundary, ΔT_c^χ does not exceed 6 K while it is almost twice as large in YBCO.[8-10] In the more oxidized samples $\Delta T_c^\chi \leq 1$ K, like ΔT_c^R in YBCO.[11] It is noted that the O_2-quenched samples exhibit the lowest magnetic transition width, implying good homogeneity of the grain-boundary weak-link network. Interestingly, ΔT_c increases monotonically with decreasing oxygen content almost independently of x (Fig. 4). This suggests that the oxygen content and distribution, rather than the cation composition, are the major causes for transition broadening. We have also observed that the larger ΔT_c^χ,
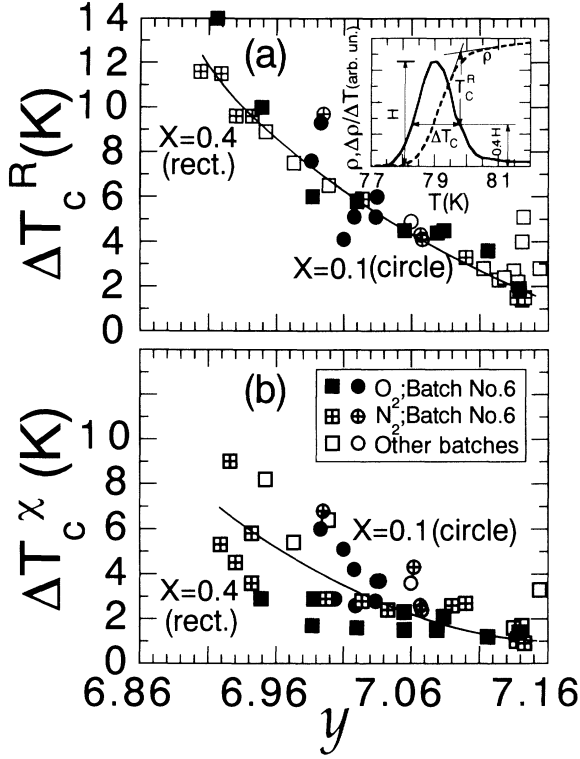
FIG. 4. Width of (a) the resistive ΔT_c^R and (b) the magnetic ΔT_c^χ transition as function of oxygen content y. Inset demonstrates the method of determination of ΔT_c^R.

the wider becomes the tail in the resistive transition (not shown). This tail, which develops upon increasing the measurement current, reflects the contribution of grain boundaries to the resistivity.[6] This observation confirms that the susceptibility transition is associated with grain boundaries.

In most samples, $\Delta T_c^\chi < \Delta T_c^R$ (Fig. 4). In particular, for the O_2-quenched samples, ΔT_c^χ might be as small as $\frac{1}{3}\Delta T_c^R$. The narrow magnetic transition could reflect a narrow distribution of T_c in the network of weak superconductor grain boundaries. The wider resistive transition might be related to the distribution of T_c inside (or among) the grains. It is therefore possible that under the best reduction conditions employed in this investigation there still remains slight oxygen inhomogeneity inside grains, particularly at low y where ΔT_c^R is large. We estimate an upper limit of this inhomogeneity by employing the criterion of Jacobson *et al.*[10] Using the relationship $\Delta T_c = \Delta T_c^0 + \frac{dT_c}{dy}\Delta y$, these authors have shown that, in YBCO, ΔT_c correlates with the inhomogeneity Δy within the sample. Here ΔT_c^0 denotes the "intrinsic" width induced by other effects (in fact, all except oxygen inhomogeneity). We note that, unlike in YBCO, the derivative $\frac{dT_c}{dy}$ is essentially constant. Therefore, in the present family ΔT_c^R depends linearly on Δy, implying that Δy increases at low y. Substituting for ΔT_c^0 a value of 1 K [i.e., on the order of the lowest ΔT_c^R ($\cong$ 1.5 K), see Fig. 4(a)], and for $\frac{dT_c}{dy}$ the average value 300 K per oxygen obtained from Fig. 3(a), we obtain $\Delta y \cong \pm 0.015$ in the
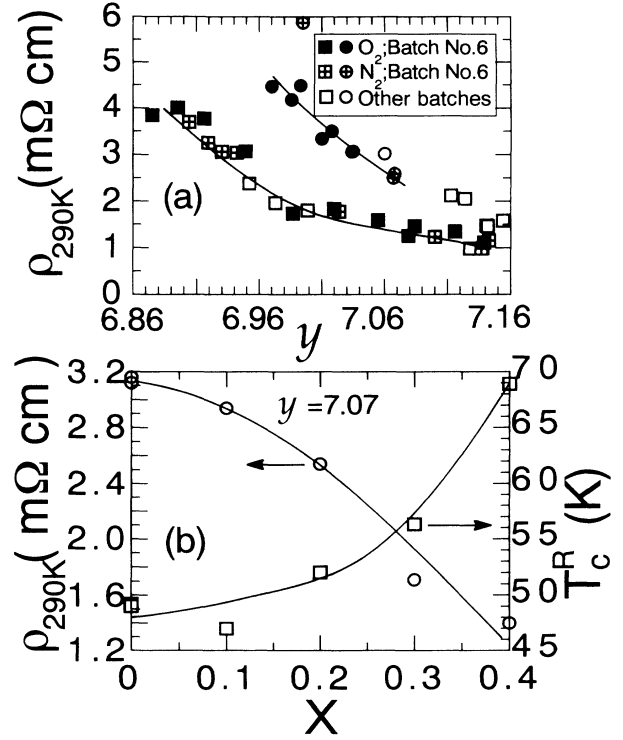
FIG. 5. (a) Room-temperature resistivity $\rho_{290\,K}$ as a function of oxygen content y. Circles denote $x = 0.1$ and rectangles denote $x = 0.4$ samples. (b) $\rho_{290\,K}$ and T_c^R (resistivity-onset transition) extracted at constant oxygen content ($y = 7.07$) as a function of composition x. This figure contains data corresponding to compositions not shown in previous figures.

worst case (e.g., corresponding to $\Delta T_c^R = 10$ K.) This value is quite low and becomes much smaller when ΔT_c^R decreases. This supports our claims for high accuracy in the determination of y.

The room-temperature resistivity $\rho_{290\,K}$ is displayed in Fig. 5(a) as a function of oxygen content for $x = 0.4$ and $x = 0.1$. The monotonic increase in ρ with decreasing y correlates with the decrease in T_c. Interestingly, ρ increases with decreasing x *even at constant* y. This is demonstrated in detail in Fig. 5(b) where $\rho_{290\,K}$ of samples with various compositions x has been extracted at $y = 7.07$. This change in $\rho_{290\,K}$ resembles the change in T_c at constant y. For convenience we also show in Fig. 5(b) the results of T_c^R vs x at this value of y. Notice that this figure also contains data corresponding to compositions not shown earlier in this investigation.

IV. DISCUSSION

The $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ family, which belongs to the 1:2:3 system, is characterized by a constant charge Q of the noncopper cations due to equal amounts of substitutions on both the Y and Ba sites, i.e., $Q = 1.75 \times 2 + 1.25 \times 3 = 7.25$ electron charges per formula unit. Here, 1.75 is the total (Ca,Ba) content of valence +2, while 1.25 is the total La content of valence +3.

Thus, exact charge compensation on the Y and Ba sites maintains the total cationic charge constant, independent of x. Therefore, when the oxygen content y is kept constant, the total anionic contribution to the charge density remains constant as well. Hence, the balance charge on the copper ions together with the average charge p per copper is constant. Under these conditions, the system becomes *isoelectronic*. It was expected that the mobile hole density per CuO_2 plane p_{plane}, which depends on the anionic and cationic contributions to the charge density, would remain constant. Hence, T_c is expected to remain constant. For instance, the well-known parabolic relationship[12] attributes a definite value of T_c to a given value of p_{plane}. In particular, $T_{c,max}$, the maximal value that T_c attains, occurs at $p_{plane} = 0.16$.[12] In contrast, we show here that in the present family one cannot predict the value of T_c based solely on the apparent value of p_{plane}. This is demonstrated by comparison of the $T_c(y)$ curves for various compositions (Fig. 3) and observation of the changes in T_c at constant p_{plane} [Fig. 5(b)]. For instance, at $y = 7.05$ both T_c^R and T_c^χ change by 21 K with x varying from 0.1 to 0.4. At $y = 7.00$ the change in T_c is even bigger (24 K). Thus, under conditions where p_{plane} seems to be constant, e.g., $p_{plane} \cong 0.16$ (see below) where in other families $T_c = T_{c,max}$, we observed a change of $\sim 30\%$ in T_c when the composition changes. We conclude that charge-compensating cosubstitutions provide a unique tool for investigating changes in mobile hole density that are not directly derived from the formal ionic charges.

The unusual behavior of the present family can be illustrated by placing our data points on a plot of $T_c/T_{c,max}$ vs p_{plane}. Recently, Zhang and Sato[13] have suggested that such a plot produces a universal relationship since curves corresponding to many p-type cuprate superconductor systems all coalesce into a single trapezoidal curve. In contrast, the present family departs markedly from the universal curve[14] since this curve does not
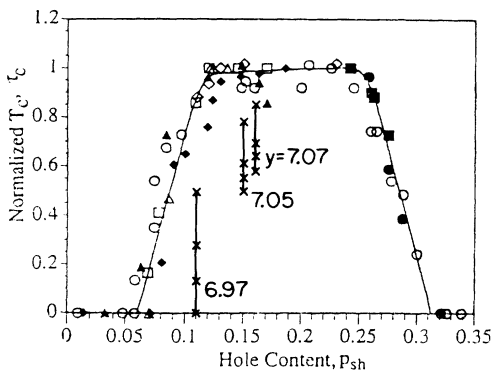

FIG. 6. The dependence of τ_c ($= T_c/T_{c,max}$) on mobile hole density per CuO_2 plane p_{plane} ($= p_{sh}$; reproduced from Ref. 13). The vertical lines correspond to samples of the present family, each having various x ($x = 0.1, 0.2, 0.3,$ and 0.4 from bottom to top) and constant oxygen content y. The three lines correspond to $y = 7.07, 7.05,$ and 6.97. The present family cannot be described by the curve corresponding to the other families.

permit big changes in T_c at constant p_{plane}, as we observed between $(Ca_{0.1}La_{0.9})(Ba_{1.65}La_{0.35})Cu_3O_{7.07}$ and $(Ca_{0.4}La_{0.6})(Ba_{1.35}La_{0.65})Cu_3O_{7.07}$ [see Fig. 5(b)]. This departure is demonstrated in Fig. 6 which reproduces Fig. 1 in Ref. 13. The endpoints on each of the three vertical lines are the results of both materials mentioned above (i.e., the $x = 0.1$ and $x = 0.4$ samples), measured at three different isoelectronic charge densities, corresponding to $y = 7.07, 7.05,$ and 6.97. To each line we assigned a value of p_{plane} derived from the formula of Tokura *et al.*[15] [$p_{plane} = \frac{1}{2}(y - Q + \frac{1}{2})$], which for $y = 7.07$ yields the value 0.16 that we use above. We took $T_{c,max} = 81.5$ K for all x members of this family.[14] We emphasize, though, that as long as p_{plane} is taken to be a function of only y and Q, it does not make any difference what the exact formula for determining p_{plane} is, since p_{plane} remains constant when both y and Q do. Thus our conclusion about big variation of T_c at constant p_{plane} remains valid *irrespective* of the method employed for its estimate. Clearly, these vertical lines (Fig. 6) cannot be described by the trapezoidal curve as can other materials. Apparently, under isoelectronic conditions the mobile hole density is not directly related to the chemical valence of the ions.

The increase in the mobile hole density would usually be accompanied by a decrease in room-temperature resistivity. Indeed, at $y = 7.07$, the resistivity of the $x = 0.1$ samples is almost twice larger than that of the $x = 0.4$ samples (Fig. 5). We emphasize that this increase in ρ occurs under isoelectronic conditions (constant y). However, changes in scattering lifetime may also contribute to this large change in resistivity.

Hints for peculiarities in the dependence of T_c on hole density have been reported recently in a similar cosubstituted family $(Ca_xY_{1-x})(Ba_{2-x}La_x)Cu_3O_y$. In this family, investigated by Slater and Greaves,[4] Q is kept constant ($Q = 7$) and y was determined from neutron diffraction. These authors suggest a "redistribution of electrons from Cu(2) to Cu(1)" as a possible explanation of their results.

Our observations suggest that, while the average electron density remains constant, the chemical changes induce changes in band structure, thereby modifying the actual mobile hole density. In particular, upon passing from the low-x to the high-x members, the Fermi energy E_F shifts downward relative to the top of the conduction band, yielding large increase in the hole density. Any formula attempting to estimate the actual hole density should take these changes in band structure explicitly into account.

In support of substantial changes in band structure in this family as a function of x, notice that the oxygen content at which the MI transition occurs increases with decreasing x. This confirms our suggestion that E_F of the low-x members lies closer to the top of the band, thus requiring fewer electrons (i.e., a smaller oxygen deficit) to drive these materials from the superconductor into the insulator state. As the absolute position of E_F is not expected to change with x (since, after all, the total electron density does not change at constant y), this would require a change in band structure.

Still another indication of substantial changes in the electronic density of states (DOS) $N(E)$ in this family is the range in oxygen content within which superconductivity disappears, i.e., $\Delta y \cong 0.25$. Compared with YBCO in which $\Delta y \cong 0.6$, the range of existence of the superconducting phase is about two to three times narrower. One would expect that in the present family the MI transition would occur at $y \cong 6.65$ (i.e., since $Q = 7.25$ as compared to $Q = 7$ in YBCO).[16] Instead, it occurs at $y \cong 6.9$, implying that the superconducting state is extremely sensitive to oxygen depletion. Such a sensitivity to small changes in electron density is typical of narrow-band behavior,[17-19] or of the behavior in the vicinity of a Van Hove singularity in the DOS.[20] A similar behavior was observed in $ErBa_{1.7}La_{0.3}Cu_3O_y$,[21] where the MI transition occurs at $y \cong 6.8$ and in $La(Ba_{2-x}La_x)Cu_3O_y$.[22,23] As in the present family, these materials contain La on the Ba site. This suggests that the substitution of La for Ba may have a strong effect on the electronic properties in these systems. In comparison with YBCO, this seems to reflect substantial sharpening of the DOS (i.e., larger dN/dE) at the upper leading edge of the conduction band, that is, in the energy range below the top of the band. Similar conclusions have been obtained by comparing $LaBa_2Cu_3O_7$ ($T_c = 92$ K) with our $x = 0$ member.[1]

La_{Ba} (La that substitutes for Ba) is believed to play an important role not only as an electron donor but also as a center around which oxygen tends to accumulate in the basal plane. This tendency of oxygen to accumulate is reflected in the large y values and in the tetragonal structure. We note that, in most of the range in which this family is superconducting, the oxygen concentration exceeds the maximal y attainable in YBCO. In part, this could be related to the large value of Q in this family. Thus the analog of $y = 7$ in YBCO is, in the present case, $y = 7.125$. However, in YBCO it is hard to obtain $y > 6.98$ whereas in the present case we got $y = 7.15$ at $x = 0.4$. Turning to the tetragonal structure, notice that any oxygen in excess of $y = 7$ has to increase the O(5) site occupancy [where O(5) denotes the empty site in an ordered chain YBCO], thereby increasing the tendency toward a tetragonal structure. Clearly, if $y = 8$ had been accessible, the material would be perfectly tetragonal even on a local scale.

The concentration of La_{Ba} ($= 0.25 + x$) increases with composition. Thus, even at constant y there is a tendency of oxygen to accumulate around these La_{Ba} centers. Hence, with increasing x, *oxygen redistribution within the basal plane* is expected, in which oxygen accumulates around La_{Ba} and, to a lesser extent, depletes around Ba. It is our conjecture that this oxygen redistribution is the major cause for the changes in band structure at constant y. It should also provide localized states to the band made of basal-plane orbitals, which act as electron traps and accept a fraction of the electrons donated by the La_{Ba}. The remaining fraction is insufficient to fully compensate for the hole that is generated in the CuO_2 plane by electron transfer to the Ca_Y (Ca that substitutes on the Y site). The net effect is an additional internal electron transfer from planes to "chains"

(i.e., in addition to charge transfer that may be caused by nonisovalent substitution). Internal electron transfer would be consistent with the decrease in a (lattice parameter) owing to the antibonding nature of the CuO_2 band states; it is known that removal of electrons from such states causes a decrease in lattice parameter.[24]

It is noted that, in order to explain the large anisotropy in the temperature factors of the chain oxygen, Slater and Greaves[4] assumed a static inward shift of oxygen toward the center of the basal plane. They notice that this shift is related to the presence of La on the Ba sites, as it is large in the vicinity of La_{Ba} and completely absent in the vicinity of Ba, thereby giving rise to disorder in the basal plane. It is possible that this kind of disorder also contributes to changes in the band structure.

Charge redistribution might be important also in another well known problem within the 1:2:3 system, namely, the puzzle of the effective valence of Pr (i.e, whether it is $+3$, $+4$, or somewhere in between). Recently, Khomskii[25] has suggested that in $(Pr_xY_{1-x})Ba_2Cu_3O_7$ internal charge transfer between CuO_2 planes and the charge reservoir is the dominant factor in controlling T_c. Presenting spectroscopic evidence that the valence of Pr is close to $+3$, independent of x, he has attributed the disappearance of superconductivity to charge redistribution effects, presumably induced by the extra positive charge on the Pr (i.e., in excess of $+3$). Since this happens at almost constant y, this family would again be in marked deviation from the universal behavior demonstrated by other systems.

V. CONCLUSIONS

By careful oxygen reduction we have shown that two distinct $T_c(y)$ and $\rho(y)$ curves are obtained for $x = 0.1$ and $x = 0.4$. The large increase in T_c and decrease in ρ under isoelectronic conditions (i.e., at constant oxygen content), is unexpected. It signals additional electron transfer from planes to "chains" that takes place despite the average hole density being constant. We have associated this internal charge transfer with changes in band structure believed to be related to the accumulation of oxygen in the vicinity of La_{Ba} and to addition of Ca_Y.

Decrease in the value of y at the MI transition with increasing x provides supportive evidence for changes in band structure. In particular, an upward shift of the top of the conduction band yields an increase in mobile hole density, equivalently described in terms of electron transfer. Similarly, the decrease in lattice parameters supports internal electron transfer.

In comparison with YBCO, the narrow region of superconductivity in the present family ($\sim 6.9 \le y \le\sim 7.15$) suggests substantial sharpening in the density of states at the top of the conduction band. Lack of a plateau in the dependence of T_c on y suggests that oxygen ordering is relatively unimportant in the present family, in harmony with the tetragonal structure.

The big changes in T_c and ρ that take place at apparently constant hole density suggest that conventional methods for estimating the mobile hole density should be reexamined. In particular, these methods should be

modified to allow for changes in hole density when the chemical count of electrons (or holes) gives a fixed value. Through other cosubstitutions, we are currently investigating additional families. Our preliminary results with Nd replacing La suggest that similar effects occur.

[1]D. Goldschmidt, G.M. Reisner, Y. Direktovitch, A. Knizhnik, E. Gartstein, G. Kimmel, and Y. Eckstein, Phys. Rev. B **48**, 532 (1993); Physica C **217**, 217 (1993).

[2]F. Keller-Berest, S. Megtert, G. Collin, P. Monod, and M. Ribault, Physica C **161**, 150 (1989).

[3]H. Gu, K.K. Fung, C.D. Wei, J.L. Zhang, and D.L. Yin, Physica C **208**, 391 (1993).

[4]P.R. Slater and C. Greaves, Supercond. Sci. Technol. **5**, 205 (1992); **2**, 5 (1989).

[5]A. Knizhnik, Y. Direktovitch, D. Goldschmidt, and Y. Eckstein, Supercond. Sci. Technol. **6**, 209 (1993).

[6]D. Goldschmidt, Phys. Rev. B **39**, 2372 (1989); **39**, 9139 (1989).

[7]H. Claus, M. Braun, A. Erb, K. Röhberg, B. Runtsch, H. Wühl, G. Bräuchle, P. Schweib, G. Müller-Vogt, and H. v. Löhneysen, Physica C **198**, 42 (1992).

[8]T. Graf, G. Triscone, and J. Müller, J. Less-Common Met. **159**, 349 (1990).

[9]R.J. Cava, A.W. Hewat, E.A. Hewat, B. Batlogg, M. Marezio, K.M. Rabe, J.J. Krajewski, W.F. Peck, Jr., and L.W. Rupp, Jr., Physica C **165**, 419 (1990).

[10]A.J. Jacobson, J.M. Newsam, D.C. Johnston, D.P. Goshorn, J.T. Lewandowski, and M.S. Alvarez, Phys. Rev. B **39**, 254 (1989).

[11]D. Goldschmidt and Y. Eckstein, Physica C **200**, 99 (1992).

[12]J.L. Tallon and N.E. Flower, Physica C **204**, 237 (1993).

[13]H. Zhang and H. Sato, Phys. Rev. Lett. **70**, 1697 (1993).

[14]D. Goldschmidt, Y. Direktovitch, A. Knizhnik, and Y. Eckstein, Phys. Rev. Lett. **71**, 3392 (1993).

[15]Y. Tokura, J.B. Torrance, T.C. Huang, and A.I. Nazzal, Phys. Rev. B **38**, 7156 (1988).

[16]In the present family, $p = 0$ when $y = 6.75$. This should be compared to $y = 6.5$ in YBCO. Since, however, the actual MI transition in YBCO occurs at an oxygen content about 0.1 lower (i.e., at $y = 6.4$), we deliberately subtracted this amount from $y = 6.75$ to obtain 6.65 for the expected MI transition in the present family.

[17]J. Genossar, B. Fisher, I.O. Lelong, J. Ashkenazi, and L. Patlagan, Physica C **157**, 320 (1989).

[18]B. Fisher, J. Genossar, I.O. Lelong, A. Kessel, and J. Ashkenazi, J. Supercond. **1**, 53 (1988); B. Fisher, J. Genossar, L. Patlagan, I.O. Lelong, and J. Ashkenazi, Physica C **162-164**, 1207 (1989).

[19]J. Ashkenazi, D. Vacaru, and C.G. Kuper, in *High-Temperature Superconductivity*, edited by J. Ashkenazi *et al.* (Plenum, New York 1991), p. 569; J. Ashkenazi and C.G. Kuper, in *Studies of High Temperature Superconductors*, edited by A. Narlikar (Nova Science, New York, 1989), Vol. 3, p. 1.

[20]C.C. Tsuei, Physica A **168**, 238 (1990); D.M. Newns, H.R. Krishnamurthy, P.C. Pattnaik, C.C. Tsuei, C.C. Chi, and C.L. Kane, Physica B **186-188**, 801 (1993).

[21]D. Wagener, M. Buchgeister, W. Hiller, S.M. Hosseini, and K. Kopitzki, Supercond. Sci. Technol. **4**, S211 (1991).

[22]D.B. Mitzi, P.T. Feffer, J.M. Newsam, D.J. Webb, P. Klavins, A.J. Jacobson, and A. Kapitulnik, Phys. Rev. B **38**, 6667 (1988).

[23]S.A. Sunshine, L.F. Schneemeyer, J.V. Waszczak, D.W. Murphy, S. Miraglia, A. Santoro, and F. Beech, J. Cryst. Growth **85**, 632 (1987).

[24]J.B. Goodenough, Supercond. Sci. Technol. **3**, 26 (1990).

[25]D. Khomskii, J. Supercond. **6**, 69 (1993).