PHYSICAL REVIEW B VOLUME 48, NUMBER 1 1 JULY 1993-I

Tetragonal superconducting family $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$: The effect of cosubstitution on the transition temperature

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(Received 29 September 1992; revised manuscript received 25 January 1993)

We have prepared a family $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ within the 1:2:3 high-temperature-superconductor system in which Ca occupies solely the Y site while La partly occupies the Y site and partly the Ba site. This family is characterized by constant charge (7.25) of the noncopper cations via compensating substitutions. It is tetragonal throughout the single-phase-existence range $0.0 \leq x \leq 0.5$. Attempts to prepare $CaLaBaCu_3O_7$ were unsuccessful yielding the $x=0.5$ member as a major phase and impurity phases. We have determined atomic positions and occupancies by Rietveld refinement of x-ray powder-diffraction data, and oxygen stoichiometry by iodometric titration. A *double-plateau* behavior in transition temperature (T_c) vs cation concentration (x), very similar to the T_c vs δ variation in $YBa_2Cu_3O_{7-\delta}$, has been observed. Albeit, oxygen stoichiometry is *almost constant* (i.e., $y \cong 7.1$) between both plateaus in the present family. Besides, the transition width *decreases* with increasing x. We have examined several known models that attempt to correlate T_c with chemical and structural parameters, including models that deal with ordinary charge transfer, bond-valence sums, interlayer distance, and oxygen-ordered domains. We propose that in materials in which compensating substitution takes place, *additional* charge transfer is responsible for the increase in hole concentration in the planes, yielding increase in T_c with increasing x. Specifically, besides ordinary electron transfer from planes to "chains" at $x=0$, there exists (at $x>0$) an additional electron transfer from the planes to the Ca. At the same time, electron transfer from the La (on Ba site) to the planes does not fully compensate for the transfer to the Ca since some of the electrons go from the La to the "chains." The La (on Ba site) is believed to play an important role in charge transfer, structure determination, and band-structure changes through its tendency to attract oxygen to the plane of the chains.

I. INTRODUCTION

Many materials of the 1:2:3 system have the orthorhombic structure. Until the discovery of tetragonal high-temperature superconductors (HTSC), many investigators considered the orthorhombic distortion in the *ab* plane to play an important role in superconductivity. One of the first 1:2:3 tetragonal HTSC materials, having $T_c \cong 80$ K, has been claimed to be $CaLaBaCu_3O_7$. Despite several recent reports on the existence of a phase with this composition, we have failed to produce it. Instead, and starting from a nominal mixing ratio of Ca:La:Ba=1:1:1, we have identified (by x-ray powder diffraction) a tetragonal phase of the 1:2:3 type. However, the original 1:1:1 mixture contained, besides the above phase, also Ca_2CuO_3 as an impurity phase; no impurity phase containing Ba or La has been identified. A multiphase Rietveld refinement of the 1:1:1 mixture yielded an occupancy factor of the $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ site [the Y site in $YBa_2Cu_3O_{7-\delta}$ (YBCO)] close to 0.5 Ca/0.5 La (all the barium being assumed to be located at the barium site). The refinement showed no substantial amount of Ca on the Ba site. We therefore concluded that the material with nominal composition $CaLaBaCu_3O_{7-\delta}$ is a mixture of predominantly $(Ca_{0.5}La_{0.5})(Ba_{1.25}La_{0.75})Cu_3O_{7-\delta}$ and Ca_2CuO_3. In order to substantiate this conclusion we have prepared a new mixture (i.e., Ca:La:Ba =0.5:1.25:1.25) according to this composition. This material has been identified as *a single tetragonal phase* with no measurable amounts of impurity phases, having lattice parameters identical to those reported for the 1:1:1 material. We want to emphasize that all impurity lines that appeared in the original 1:1:1 mixture have disappeared in this preparation (see Fig. 1).

We subsequently encountered a paper by Keller-Berest *et al.*,[1] which had apparently passed unnoticed by successive investigators, making exactly the same claims regarding the phase composition, structure, and impurity-phase content of the 1:1:1 mixture. Our results thus provide an independent check of theirs. We therefore suggest that $CaLaBaCu_3O_7$ does not exist as a single phase under ordinary preparation conditions, and that conclusions drawn on multiphase materials in this family should be reexamined.

Notably, $(Ca_{0.5}La_{0.5})(Ba_{1.25}La_{0.75})Cu_3O_7$ has $Q=7.25$, Q denoting the average formal charge on the noncopper cations. It occurred to us that, since the 1:1:1 mixture apparently selects this material as the most stable phase, it could be a representative member of a family with a varying amount of Ca on the Y site but with constant Q, that would form easily. On the other hand, $LaBa_2Cu_3O_7$ which could be an end member of such a family (i.e., containing no Ca), but with $Q=7$, does not form easily. Hence, we have attempted to prepare the family

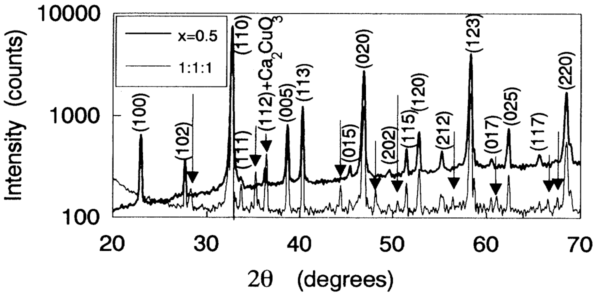

FIG. 1. X-ray powder-diffraction spectra of the pure $x=0.5$ member $(Ca_{0.5}La_{0.5})(Ba_{1.25}La_{0.75})Cu_3O_y$ and of the multiphase 1:1:1(=Ca:La:Ba) mixture. Presentation of the intensity on a logarithmic scale emphasizes low-intensity impurity lines. Ten impurity lines that correspond to Ca_2CuO_3 (marked by arrows) appear in the second spectrum but not in the first. Note that the strongest Ca_2CuO_3 line coincides with the (112) line of the 1:2:3 structure.

$(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ preserving $Q=7.25$ throughout its range of existence, i.e., by maintaining a fixed amount of 1.25 La atoms per formula. Keeping both Q and y constant, it was hoped that effects due to charge *distribution* (rather than to net charge variation) could be addressed. We have found that this family exists as single phase in the region $0.0 \leq x \leq 0.5$; that it is tetragonal throughout its existence range; that y almost does not vary with x; and that the transition temperature (T_c) varies from ~ 80 K at $x=0.5$, to ~ 45 K at $x=0.0$, in a manner reminiscent of the double-plateau behavior of T_c vs δ in $YBa_2Cu_3O_{7-\delta}$.

Another investigation has recently been published by Mertelj *et al.*[2] on the more extended $Ca_xLa_{1+z}Ba_{2-x-z}Cu_3O_y$ family; it contained between 0.9 and 1.4 La atoms (including our La composition at $z=0.25$) and $x=\frac{1}{3}$, $\frac{2}{3}$, or 1 Ca atoms per formula unit. At high Ca concentrations ($x=\frac{2}{3}$ and 1), it has been noted by that group that some of the materials contain Ca_2CuO_3 and $CaCu_2O_3$ impurity phases.[2] Note that their results for $x=\frac{2}{3}$ and 1 yield the same lattice parameters and atomic occupancy factors, suggesting that the major phase in both materials is identical. We conclude that one could not introduce these large amounts of Ca in this structure. This is in agreement with the upper limit of Ca occupancy on the Y site (i.e., $x \cong 0.5$) that has been obtained in this work and in Ref. 1.

II. EXPERIMENT

A. Sample preparation

Ceramic samples with nominal composition $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ have been prepared by the solid-state reaction route, with x varying in the range 0.0–1.0. Stoichiometric amounts of $CaCO_3$, La_2O_3, $BaCO_3$, and CuO, all 99.9% pure or better, have been mixed after predrying at 200 °C. La_2O_3, known to form $La(OH)_3$ at room temperature,[3] has been fired at 1100 °C for several days, removed hot and weighed before substantial reaction with water occurred. The mixtures were fired in air at 950 °C for 1–2 days and reground. The firings and grindings were repeated three times. (We once also tried firing the $x=0.5$ compound at 920 °C; no changes in properties have been observed.) At this stage, powders were found to be single phase for $0.0 \leq x \leq 0.5$ and to contain impurity phases for $0.5 < x \leq 1.0$. After pelletizing, samples were sintered 60 h at 960°C in flowing oxygen and cooled at 10 °C/h to room temperature in an attempt to provide fully oxidized samples.

We have tried two techniques for the initial grinding of raw powders, and found a remarkable difference, both in terms of oxygen stoichiometry and physical properties. In the first technique, we utilized thorough hand grinding with an agate mortar and pestle. This resulted in $y \cong 7.0$ and in relatively high resistivity of the low-x samples. In the second technique, the raw powders were ground by a machine (ZrO_2 ball mill). This process has been carried out under Ar, thereby minimizing exposure to moisture in air. This resulted in an average increase in oxygen content by ~ 0.1 and lower resistivities. Presumably the smaller particle size produced by machine grinding improves the overall reaction of the raw powders and assists oxygen incorporation. We consider materials prepared by machine grinding to represent a better quality of these materials and, unless otherwise stated, our results are for samples prepared by machine grinding.

In the bar-pressed samples used for four-probe dc resistivity measurements, we utilized gold-wire implanted electrodes. The ac susceptibility measurements were performed at 79 Hz and a driving field of the order of $\frac{1}{2}$ Oe. Disk-shaped samples were used for magnetic susceptibility. Several batches with $0.0 \leq x \leq 0.5$ were prepared and the results were fully reproducible. Care was taken to avoid effects of aging on resistivity and on oxygen stoichiometry.

B. X-ray diffraction

Powder and pellet samples were characterized by x-ray powder diffraction (Siemens D-5000 diffractometer, Cu K_α radiation). For the compounds with $0.0 \leq x \leq 0.5$, about 40 lines corresponding to the 1:2:3 structure were observed by a step scan (0.02° per 8 sec. step) in the range $6° \leq 2\theta \leq 150°$. *All* the lines could be indexed in terms of a tetragonal lattice. We emphasize that no lines remained unidentified, and that no other lines were observed, i.e., these materials are mostly single phase. Presintered powders (i.e., after three firings) have also been checked for possible changes of lattice parameters; the only observable difference was a systematic increase in the c axis (by $\sim 0.3\%$), probably due to lower oxygen stoichiometry (by ~ 0.1). For $0.6 \leq x \leq 1.0$ we obtained, besides the above lines, several additional lines corresponding to impurity phases among which we have identified Ca_2CuO_3 and CaO; their amount increased with x. However, some impurity lines remained unidentified. Following Keller-Berest *et al.*,[1] we caution that these impurity phases, having smaller diffracted intensity than the main phase (which retains all the heavy elements), are not readily observable; thus *their relatively small intensity does not imply negligible concentrations.*

For the $0.0 \leq x \leq 0.5$ samples we performed an intensity analysis of the presintered powder-diffraction spectrum by the Rietveld refinement method, using the program DBWS-9006. As is well known, this iterative method requires as input an initial guess of the lattice parameters, space group, and atomic positions. Using a nonlinear fitting procedure, it is quite sensitive to the initial guess and to the number of refined parameters. Convergence to a local minimum could also become a problem. However, the present structure is isostructural with tetragonal $YBa_2Cu_3O_6$, i.e., the space group is D_{4h}^1 ($P4/mmm$, No. 123); hence the atomic positions are known. Thus we have refined the lattice parameters, the z coordinates, and the occupancy factors (OF), and have restricted the refinement to three isotropic temperature factors (corresponding to Ba and La, Cu and Ca, and O). All our Rietveld refinements converged, yielding a discrepancy factor $R \cong 8\%$. We have tried two different line-shape functions in the intensity profile fitting, but this had no significant effect on the results. All Debye-Waller temperature factors came out essentially nonnegative, providing additional confidence in the procedure.

C. Iodometric titration

We have made careful iodometric titration under still Ar according to known double-titration procedures.[4] In these procedures, two titrations are required for the determination of the amount of oxygen (y) per formula unit: The first (titration A in Ref. 4) is required to determine the total amount of Cu in the sample. The second (titration B in Ref. 4) yields the amount of Cu^{3+} ions, provided that other easily reducible ions are not present. We have checked the reproducibility of this method by repeated titrations and found that the reproducibility in y can be better than 0.005 (as determined by 15 separate titrations on a large $YBa_2Cu_3O_{6.9}$ sample). The absolute accuracy in determination of y relies on the following assumptions.

(1) There exists only one phase. Our samples have been checked by x ray and found to be pure. In other words, no impurity lines can be observed under high signal conditions. In an attempt to estimate the sensitivity of our x-ray results to small amounts of impurity phases, we have examined mixtures of $BaCuO_2$ and YBCO. We found an upper limit of roughly 6% (molar) of $BaCuO_2$. This is equivalent to an underestimate of y by ~ 0.03 (e.g., one obtains $y = 6.97$ instead of 7.00). However, this adds only a systematic error provided that the amount of hypothetical impurity phases does not vary with x.

(2) The material has an exact cation ratio of 1:2:3. Single crystals of composition $(Ca_{0.4}La_{0.6})[Ba(La)]_2Cu_{2.9}O_y$ have been reported.[1] If there really were 2.9 rather than 3 Cu ions per formula unit, our assumption would overestimate y by ~ 0.1. However, in ceramics (containing undetectable amounts of impurity phases and prepared from the correct 1:2:3 nominal composition) it is unlikely that large deviations in Cu composition (as reported for crystals grown from the melt) will be observed. Therefore, we assume an exact 1:2:3 composition.

In summary, reproducibility at different x values is estimated at $\Delta y = \pm 0.005$, while absolute accuracy corresponds to an uncertainty that is roughly an order of magnitude higher.

III. RESULTS

A. Resistivity and susceptibility

1. *Hand-ground samples*

The resistivities of the various members of the $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ family, prepared by the hand-grinding procedure, are shown in Figs. 2(a) and 2(b). The trend, well known from other families, that correlates improved metallic behavior with higher T_c, is clearly observed in this family with increasing x [Fig. 2(a)]. The end member $x = 0.5$ [Fig. 2(a)] has about twice the resistivity of high-quality ceramic $YBa_2Cu_3O_7$.[5] The latter material is known to have long ordered chains that possibly make a significant contribution to conductivity.[5] The difference in resistivities then reflects chain-oxygen disorder on a length scale that is shorter than the mean free path,[5] in accordance with the tetragonal structure. At the other end [$x = 0.0$, $x = 0.1$, Fig. 2(a)] the resistivity becomes an order of magnitude larger and the temperature dependence at low temperatures becomes inverted (i.e., $d\rho/dT < 0$). This "semiconductorlike" behavior is typical of reduced YBCO when the carrier density becomes low. However, unlike in YBCO, the oxygen stoichiometry does not decrease substantially at low x values (see Sec. III C), and the net charge is almost independent of x. Thus it is not clear what is the origin of the change in conductivity and in T_c.

Notably, the transition width at small currents *increases* substantially at low-x values [Fig. 2(b); the broadening is much more pronounced than in reduced YBCO (Ref. 6)]. This is unexpected since the Ca concentration, that could be a possible source of disorder and transition broadening, decreases at low-x values. Besides, for all x values (except $x = 0.2$, 0.5), there is a strong dependence of transition width on current [Fig. 2(b)]; that is, broadening takes place over the entire transition range, beginning at the onset, not just at the tail.[7] This suggests nonuniformity related to the phase at the interior of the grains rather than at grain boundaries, since the latter usually manifests itself in the development of a tail at the end of the transition due to weak-link effects.[7] This may perhaps indicate nonuniform oxygen distribution between the interior and the boundary of a grain, despite the slow cooling rates employed in the preparation. Note also that in Fig. 2(a), the resistivity of the $x = 0.2$ sample is lower than the resistivity of the $x = 0.25$ and 0.3 samples. We have observed this on several samples of different batches. No unusual structural feature could be detected at this composition; the oxygen stoichiometry, however, presented an unusual dip in this composition range ($0.2 \leq x \leq 0.3$).

2. *Machine-ground samples*

We turn now to the resistivity and susceptibility results of the improved (machine-ground) samples [Figs. 2(c) and

2(d), and Fig. 3, respectively]. One notes in Fig. 2(c) that the metallic behavior improved dramatically particularly at low-x values. The "semiconductorlike" behavior has disappeared, implying that its origin is related to oxygen effects. Recall that machine-ground samples have more oxygen (Sec. II A). The resistivity of the $x=0.0$ sample has gone down and is now higher than the resistivity of the $x=0.5$ sample (which decreased only slightly) by only a factor of ~ 3. Still, the variation in y between the $x=0.0$ and 0.5 members ($\Delta y=0.13$, see Table I) is the same as in the hand-ground samples, again implying that the net average charge density does not vary much with x. The transition width [Fig. 2(d)] is now quite small (almost three times smaller than for the hand-ground samples). The width increases with decreasing x, implying that the trend of broadening at low x is unrelated to a particular preparation procedure. At the same time, the sensitivity of transition width to current density has disappeared. Both observations suggest that, on the one hand, the broadening at low x is related to oxygen and not to cation inhomogeneity; on the other hand, oxygen distribution in the interior of the grains is more homogeneous in machine-ground samples than in hand-ground samples. Another interesting observation is that the anomalies in resistivity, in T_c, and in y that were observed in hand-ground samples in the vicinity of $x \cong 0.2$ (Sec. III A 1) have disappeared.

The variations of T_c^R and T_c^X (the resistive and magnetic onset transition temperatures, respectively), and of the

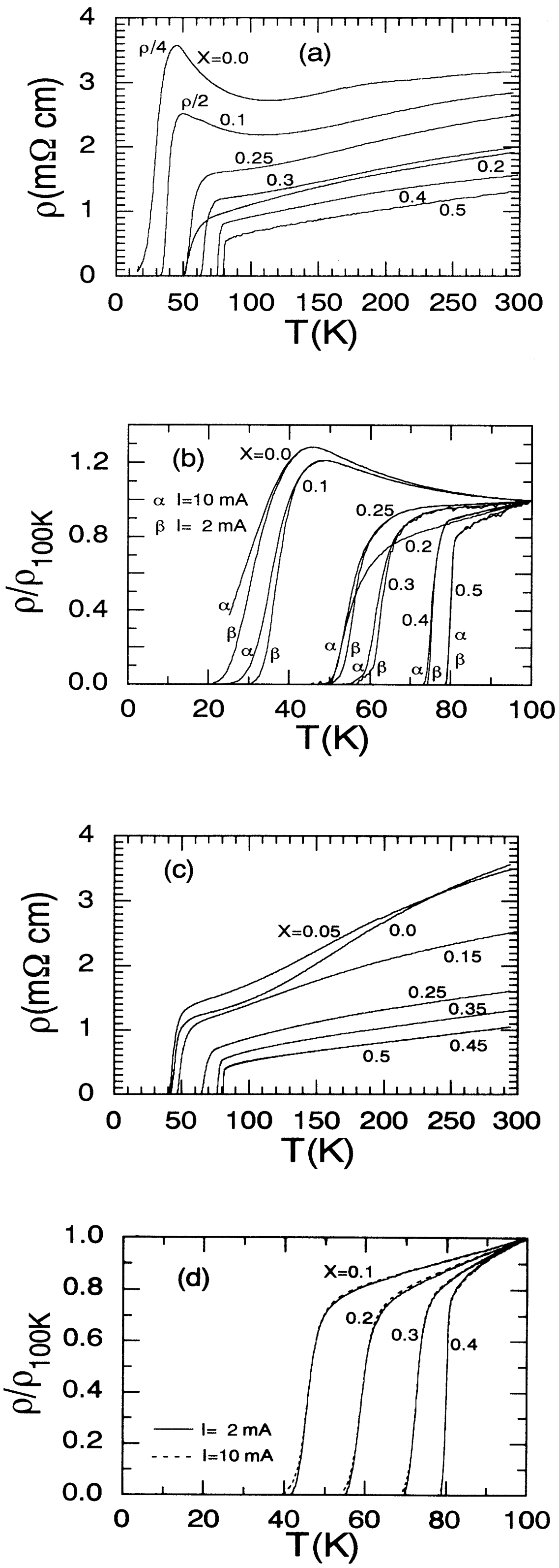

FIG. 2. Temperature dependence of resistivity at various cation compositions (x) of (a), (b) hand-ground samples, and (c), (d) machine-ground samples. (b), (d) show normalized resistivity illustrating the sensitivity of transition width to current.

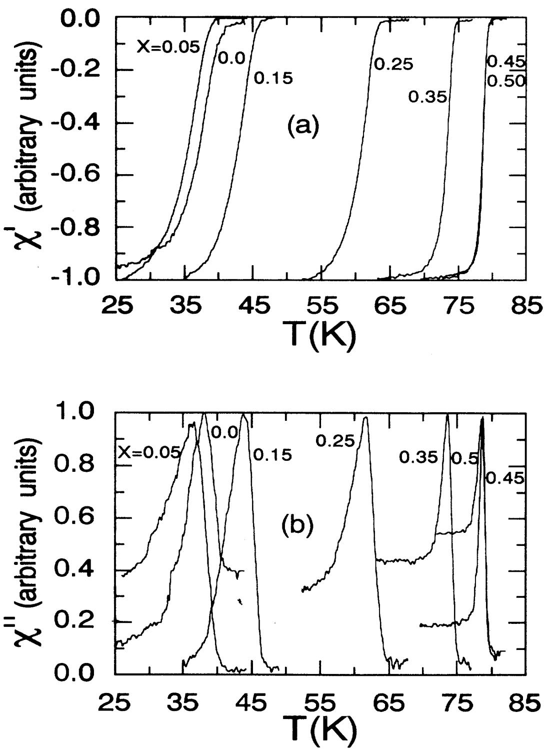

FIG. 3. (a) Real and (b) imaginary parts of the transition in ac magnetic susceptibility at various cation compositions (x), of machine-ground samples.

TABLE I. Dependence of onset transition temperature, transition width, room-temperature resistivity, and oxygen stoichiometry (y) on cation composition (x), of machine-ground samples.

x	$T_c^R(\Delta T_c^R)$ (K)	$T_c^X(\Delta T_c^X)$ (K)	$\rho_{290\ \text{K}}$ (mΩ cm)	y
0.00	47.8(5.3)	40.0(5.6)	3.54	7.007
0.05	46.7(6.1)	38.6(6.2)	3.47	7.030
0.10	48.3(5.4)	38.8(3.7)	3.02	7.060
0.15	51.9(5.1)	45.6(5.5)	2.50	7.052
0.20	61.7(5.4)	50.2(5.0)	2.53	7.082
0.25	70.0(5.4)	62.9(4.0)	1.60	7.087
0.30	74.6(3.9)	67.1(2.8)	1.92	7.110
0.35	78.5(2.6)	74.3(2.0)	1.29	7.108
0.40	80.6(1.3)	77.8(1.8)	1.48	7.141
0.45	81.4(0.9)	79.2(1.1)	1.04	7.135
0.50	81.3(0.7)	79.2(1.4)	1.04	7.137

transition widths ΔT_c^R and ΔT_c^X throughout the composition range $0.0 \leq x \leq 0.5$ are presented in Figs. 4(a) and 4(b), respectively, and in Table I. A central feature found in this work is the double-plateau behavior in T_c vs x throughout the existence range of the single phase ($x \leq 0.5$). That is, for $0.0 \leq x \leq 0.1$, $T_c^R \cong 47$ K ($T_c^X \cong 40$ K) while for $0.4 \leq x \leq 0.5$, $T_c^R \cong 81$ K ($T_c^X \cong 79$ K). Notice that the double plateau appears both in electric and magnetic measurements. This implies that the double plateau is mainly a property of the phase rather than being a weak-link (grain-boundary) effect. This dependence of T_c on x is similar to the double-plateau behavior of T_c vs δ in $YBa_2Cu_3O_{7-\delta}$. The latter has been related to a specific ordering of the oxygens (i.e., ordered chains every other unit cell).[6] However, in the present family y remains almost unchanged (see Sec. III C. The slight change in y between both plateaus is much smaller than the change in δ in $YBa_2Cu_3O_{7-\delta}$, though the changes in T_c are similar). Thus, the double-plateau behavior should be unrelated to this specific oxygen ordering. The same double-plateau behavior has been observed also for hand-ground samples, the only difference being that the lower plateau occurs at ~40 K.

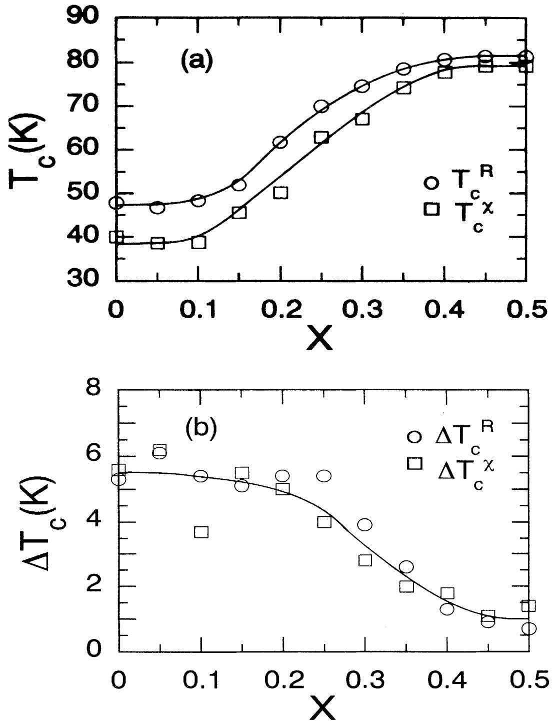

FIG. 4. Resistive and magnetic (a) onset transition temperatures (T_c^R, T_c^X) and (b) transition widths (ΔT_c^R, ΔT_c^X) at various cation compositions (x) of machine-ground samples. Notice the double-plateau behavior of T_c vs x.

B. Structure

Lattice parameters and unit-cell volume of the hand-ground samples are shown in Fig. 5 and Table II. The system is tetragonal and pseudocubic ($c = 3a$) throughout the entire existence range. In the single-phase region ($x \leq 0.5$), the lattice parameters and volume decrease monotonically with x. For compositions that have been reported by other groups,[1,2] ($x = \frac{1}{3}, 0.5$) our results are similar to theirs (at $x \cong 0.5$ they are identical[1]; at $x = \frac{1}{3}$ the results of Ref. 2 exceed ours by ~0.4%). In the multiphase region ($x > 0.5$), the lattice parameters remain practically constant reflecting the parameters of the majority phase with $x = 0.5$ [i.e., $(Ca_{0.5}La_{0.5})(Ba_{1.25}La_{0.75})Cu_3O_y$, or a closely related variant of this phase, that is, with a different La/Ba ratio on the Ba site]. It is somewhat surprising that the lattice parameters of the $x = 0.5$ sample do not lie on the linear curve corresponding to the $x \leq 0.4$ samples, but rather lie higher on the line corresponding to the $x \geq 0.6$ samples. Nevertheless, the $x = 0.5$ sample appears to be single phase.

Throughout the Rietveld analysis we have refined the lattice parameters and z coordinates (fractional coordinates in the c direction) of Ba(La), of O(3) (apical), and of Cu(2) and O(2) (in the Cu-O_2 plane). The results are summarized in Table II. We have also tried an orthorhombic

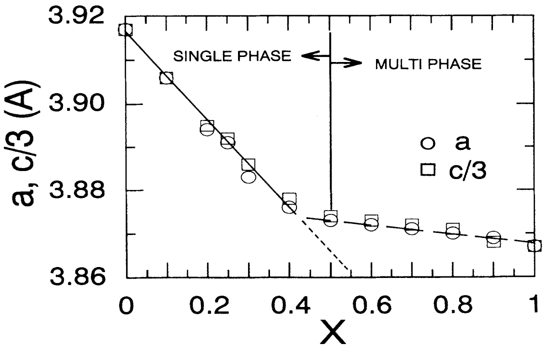

FIG. 5. Tetragonal lattice parameters (a,c/3) as a function of cation composition (x).

TABLE II. Lattice parameters, fractional atomic coordinates in the c direction (z), site occupancy factors (OF), Debye-Waller temperature factors (B), and discrepancy factors (R_I, R_{wp}) as obtained from Rietveld refinements of hand-ground and presintered powders. Lattice parameters marked by the asterisk correspond to sintered and oxygenated pellets. Numbers in parentheses are estimated standard deviations of the last significant digit. The results for $x=0.5$ are approximate (see text).

x		0	0.1	0.2	0.3	0.4	0.5
a (Å)*		3.917(1)	3.906(1)	3.894(1)	3.883(1)	3.876(1)	3.873(1)
$c/3$ (Å)*		3.917(1)	3.906(1)	3.895(1)	3.883(1)	3.878(1)	3.874(1)
V (Å^3)*		180.3	178.8	177.2	175.8	174.8	174.3
a (Å)		3.921(1)	3.910(1)	3.900(1)	3.887(2)	3.877(2)	3.876(1)
$c/3$ (Å)		3.925(1)	3.920(2)	3.908(1)	3.901(2)	3.890(1)	3.888(2)
V (Å^3)		181.1	179.8	178.3	176.8	175.4	175.3
Ca($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	(B)		0.022(5)	0.28(3)	0.46(4)	0.31(4)	0.3
La($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)	(B)	0.05(2)	0.13(2)	0.05(2)	−0.05(3)	0.11(3)	−0.1
Ba(La)	(z)	0.1845(2)	0.1846(2)	0.1848(1)	0.1837(1)	0.1835(1)	0.184
	(B)	0.05(2)	0.13(2)	0.05(5)	−0.05(3)	0.11(3)	−0.1
Cu(1) chain	(B)	0.09(4)	−0.003(8)	0.28(3)	0.46(4)	0.31(4)	0.3
Cu(2) plane	(z)	0.3469(4)	0.3491(4)	0.3478(2)	0.3495(3)	0.3498(3)	0.3503
	(B)	0.09(4)	−0.003(8)	0.28(3)	0.46(4)	0.31(4)	0.3
O(1) chain	(OF)	0.87(8)	1.003(4)	0.994(3)	0.94(7)	1.005(6)	
	(B)	0.08(4)	0.56(18)	1.77(22)	1.17(13)	1.12(20)	1.66
O(2) plane	(z)	0.3634(14)	0.3758(11)	0.3718(8)	0.3745(9)	0.3691(8)	0.3647
	(B)	0.08(4)	0.56(18)	1.77(22)	1.17(13)	1.12(20)	1.66
O(3) apical	(z)	0.1614(20)	0.1586(21)	0.1590(12)	0.1565(17)	0.1579(16)	0.1695
	(B)	0.08(4)	0.56(18)	1.77(22)	1.17(13)	1.12(20)	1.66
R_I		7.3	9.6	8.2	7.0	7.7	11
R_{wp}		8.4	8.0	6.8	7.6	7.4	9.9

initial guess according to the space group D^1_{2h} (*Pmmm*, No. 47); the refinement converged to a tetragonal structure. (This does not rule out the possible existence of short-scale orthorhombic distortions as has been suggested by neutron-diffraction studies on related materials.[8]) The refinement of the $x=0.5$ sample, on the other hand, did not converge easily and the results for that sample (Table II) are only approximate.

Another result of this calculation is the occupancy factors (OF) of the O(1) ("chain") oxygen. It is remarkable that the O(1) position is essentially fully occupied throughout the range $0.0 \leq x \leq 0.5$. Apparently, the optimal oxygen stoichiometry even before prolonged sintering is a material with $y \cong 7$.

Our calculations could not distinguish between 0% and ~20% of the Ca being placed on the Ba site (this is probably the result of an increased number of fitting parameters). Our further indirect evidence that Ca is located mostly on the Y site (as was claimed in Ref. 1) comes from the decrease (3%) of the interplane [Cu(2)-Cu(2)] distance when x varies from 0.0 to 0.5. This is compatible with the smaller size of Ca^{2+} (1.12 Å) as compared to La^{3+} (1.16 Å). Both sizes were taken for ions that substitute on the Y site, i.e., with eight surrounding oxygens.

We have not refined the occupancies of the Ba and La ions on the Ba site. Owing to their close atomic numbers, these atoms are indistinguishable under x rays. Our determination of the cation distribution relies on the assumption that Ba occupies solely its own site ($\frac{1}{2}\frac{1}{2}z$). Since the ionic radius of Ba^{2+} (1.5 Å) is much larger than the average rare-earth ionic size (~1.1 Å), its substitution on the Y site would cost much elastic as well as electrostatic energy. Hence, La shares both the Y and the Ba sites in proportions corresponding to the chemical formula of this family.

We have not attempted to determine the accurate location of the boundary between the single-phase and multiphase regimes. Notice that in the hand-ground $x=0.5$ sample, we could not detect impurity phases. Nevertheless, the $x=0.5$ sample lies on the line corresponding to the multiphase regime (Fig. 5) and the Rietveld refinements of this sample did not converge easily. Besides, our machine-ground $x=0.5$ sample did show traces of impurity phase while the $x=0.45$ did not. Thus the boundary of the single-phase regime probably lies slightly below $x=0.5$.

C. Oxygen stoichiometry

The variation in T_c and double-plateau behavior could, in principle, be a result of a change in cation composition (x), oxygen stoichiometry (y), or both. In order to address this issue we have done careful oxygen stoichiometry determination in variously prepared samples. Specifically, we have introduced some additional oxygen into the low-x (i.e., low-y) samples, and have reduced the oxygen from the high-x (highest-y) samples. Our conclusion is that, while there is certainly an effect of increasing T_c with increasing y, at least one half of the variation of T_c between both plateaus is due to change in

x and would also occur at strictly constant y.

The results of iodometric titrations on freshly prepared machine-ground samples, prepared under the procedure described in Sec. II A, are summarized in Table I and shown in Fig. 6. There is a small linear increase in oxygen stoichiometry with increasing x, from $y=7.01$ at $x=0.0$ to $y=7.14$ at $x=0.5$. This small change in y (i.e., $\Delta y=0.13$) should be compared with the 0.5 change in δ in $YBa_2Cu_3O_{7-\delta}$ upon transition from one plateau to the other.

We would like to emphasize that, under a given preparation procedure, the materials are believed to exhibit a unique relation between T_c and both x and y, provided that homogeneous oxygen distribution has been attained. This is a conclusion of the reproducibility of our results. (For instance, we repeated the annealing of the hand-ground samples, Sec. II A, three times and obtained results similar to those after the first anneal.) However, under different preparation conditions, we were able to increase (decrease) oxygen stoichiometry in the low-(high-)x samples resulting in a concurrent increase (decrease) of T_c. For instance, we were able to increase y to 7.05 for the $x=0.0$ sample while increasing T_c by ~10 K. Similarly, we have decreased y to 6.99 for the $x=0.4$ sample which is lower than the 7.05 value of the $x=0.0$ sample. Still, T_c decreased by only ~4 K (Fig. 7). These relatively small changes in T_c should be compared to the 34 K difference in T_c between both plateaus. Besides, one could extract from the data presented in Fig. 7 results corresponding to strictly constant y. For instance, at $y=7.05$ an increase in T_c of ~30 K between the low- and high-x members has been observed. This shows conclusively that there exist regions of oxygen stoichiometry in which T_c varies as a strong function of x whereas Q and y remain constant.

IV. DISCUSSION

We first summarize and briefly discuss our main experimental observations.

(1) The double-plateau behavior of the transition temperature as a function of Ca concentration and of La distribution (T_c vs x; recall that the concentration of La does not change with x) resembles the variation of T_c vs δ in $YBa_2Cu_3O_{7-\delta}$ upon change of oxygen stoichiometry.[6] However, via reduction and oxidation experiments we have shown that, in the present $(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$ family, changes in x contribute a major part to the variation of T_c, at least as important as changes in y. In fact, changes in y are rather small compared to YBCO. Notice the ~0.1 decrease in y in the present family as compared to the ~0.5 decrease in YBCO for the same decrease in T_c (i.e., 81–47 K and 92–58 K, respectively). In other words, the slope $\partial T_c/\partial y$ in the range where T_c varies (i.e., between plateaus) is ~500 K in the present family (Fig. 7) as compared to ~140 K in YBCO. Thus it is unclear whether or not these variations in T_c have the same origin. In particular, and since y varies only slightly and the material is tetragonal, chain ordering every other unit cell (as in $YBa_2Cu_3O_{6.5}$) is certainly *not* the cause of the double-plateau behavior in the present family.

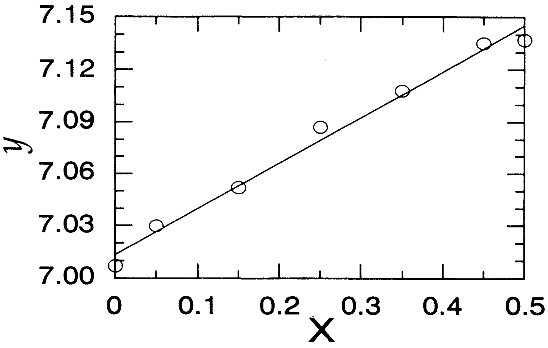

FIG. 6. Oxygen stoichiometry (y) as a function of cation composition (x), for machine-ground samples.

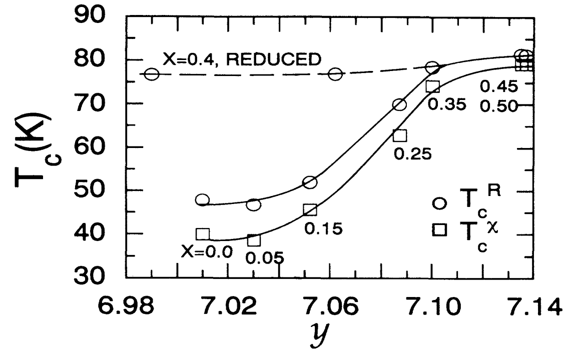

FIG. 7. Transition temperature as a function of oxygen stoichiometry for machine-ground samples. Notice the large value of $\partial T_c/\partial y$ at $y \cong 7.08$. Also notice that for a given y value (e.g., $y \cong 7.0$), T_c increases remarkably with increasing x.

(2) The slight linear increase in y with x could perhaps be related to the La_{Ba} (La that substitutes for Ba, which accounts for only a fraction of the La) concentration. Notice that together with the increase in concentration of Ca_Y (Ca that substitutes on the Y site) with x there is an increase in the La_{Ba} concentration. It has been proposed[9] that addition of La on the Ba site acts, due to the smaller size of the former, in favor of increase in the La coordination number, that is, in favor of oxygen occupation on both the O(1) (b-axis) and the would-be O(5) (a-axis) sites. This would lend itself to an increase in oxygen stoichiometry, and to a reduction in orthorhombicity. Our results are in accord with this conclusion since $y \cong 7.1$ (i.e., larger than in YBCO) and the materials are tetragonal.

(3) There is also a remarkable increase in transition width with *decreasing* x. This implies that disorder or even inhomogeneity related to the Ca_Y distribution, that probably increases with x, does not play an important role. We do not understand the decrease in ΔT_c with x; presumably it is related to the increase in y. This would imply better oxygen homogeneity at higher oxygen

stoichiometries.

In the following subsections we examine some of the common models that attempt to correlate T_c with various chemical, structural, or physical properties, in relation to our main observation, that is, *the variation of* T_c *with* x. We show that these models are not at all or not entirely applicable to the present family, raising a question regarding their general validity. In Sec. V we propose that the $\mathrm{Ca_Y}$ and $\mathrm{La_{Ba}}$ having concentrations that change with x are involved in the charge transfer thereby contributing to the variation of T_c with x.

A. Charge-transfer models

The increase in y (by ~ 0.1) in the present family is minor compared to the increase in δ in $\mathrm{YBa_2Cu_3O_{7-\delta}}$ (by ~ 0.5). Moreover, $Q=7.25$ and remains constant throughout this family via cosubstitution. Thus the average amount of $\mathrm{Cu^{3+}}$ remains unchanged (at about one $\mathrm{Cu^{3+}}$ atom/unit cell), but T_c varies significantly. Therefore, neither the oxygen stoichiometry y, nor the average cationic charge Q, is the single parameter responsible for the variation of T_c in this family.

For materials with one substitution, this point was well demonstrated by Tokura *et al.*[10] They have shown that variation of Q at constant y, or variation of y at constant Q, both cause large changes in T_c and in the boundary between normal conductors and insulators. They have proposed that a single parameter, namely, $p_{\mathrm{plane}}[=\frac{1}{2}(y-Q+\frac{1}{2})]$—the hole density associated with a single plane—incorporates all these variations. They have examined many materials with differing y and Q [belonging to the families $(\mathrm{Ca}_x\mathrm{Y}_{1-x})\mathrm{Ba_2Cu_3O}_y$ and $\mathrm{Y}(\mathrm{La}_x\mathrm{Ba}_{1-x})_2\mathrm{Cu_3O}_y$, some of which are multiphase], and concluded that T_c vs p_{plane} shows a definite pattern. We have reproduced the major pattern of their results in Fig. 8. On the same figure we added the curve corresponding to $\mathrm{YBa_2Cu_3O_{7-\delta}}$ as we have determined from the data in Refs. 6 and 11.

We have also tried to fit our data on the same figure but it clearly does not fit the other curves. The curve representing as-prepared

$$(\mathrm{Ca}_x\mathrm{La}_{1-x})(\mathrm{Ba}_{1.75-x}\mathrm{La}_{0.25+x})\mathrm{Cu_3O}_y$$

is almost a vertical line (Fig. 8). It would be exactly vertical, had y remained strictly constant. For instance, the line corresponding to $y=7.05$ ($P_{\mathrm{plane}}=0.15$)—as extracted from Fig. 7—is also shown in Fig. 8. Clearly the curves of the present work deviate significantly from the main curve representing the other materials. Particularly remarkable is the difference between the curve of the as-prepared material and that of $\mathrm{YBa_2Cu_3O_{7-\delta}}$. For the same value of p_{plane}, the difference could be as large as 40 K. The absence of any plateau in the curve corresponding to the present family in Fig. 8 reflects the rather small variation in oxygen stoichiometry as compared to YBCO. Certainly, in the present family p_{plane}, as defined above, is *not* the single important parameter. Apparently, this scheme does not take into account materials in which mutually charge-compensating substitutions are responsible for large variations in T_c. In short, this scheme is inadequate to explain our results of cosubstitution. It still remains to be shown whether p_{plane} can be redefined in some way, in order to include the case of cosubstitution.

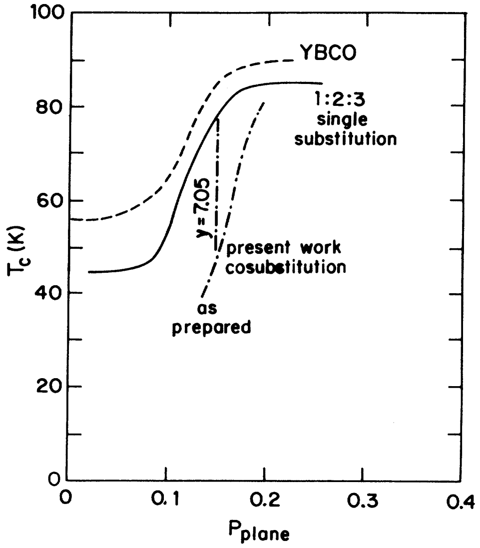

FIG. 8. Transition temperature vs number of holes per $\mathrm{CuO_2}$ plane (adapted from Ref. 10). Solid curve was taken from Ref. 10. Dashed curve is for $\mathrm{YBa_2Cu_3O_{7-\delta}}$. Dashed-dotted curve represents the as-prepared machine-ground samples in the present family. The lack of plateaus in the latter curve signifies the rather small variation in y in the present family. The vertical dashed-dotted line, corresponding to $y=7.05$ of the present family, has been extracted from the data of Fig. 7.

Through further examination of these and other materials, Manthiram and Goodenough[9] have pointed out another limitation of this model at large oxygen stoichiometries [i.e., $y \geq y_c = 6.96+\frac{1}{2}(Q-7)=7.085$ in the present family]. At these y values, and since T_c tends to *decrease* with y, trapping of *mobile* holes has been proposed, which takes place at trapping centers caused by oxygen clusters (i.e., $\mathrm{O_2^{2-}}$) in the plane of the "chains." We want to point that in this work, $y_{\max}(x=0.5)=7.15>y_c$. Therefore, either mobile hole trapping does not occur, or y_c is higher.

B. Bond-valence sums

There have been several attempts to estimate the charge distribution within the unit cell of $\mathrm{YBa_2Cu_3O_{7-\delta}}$, based on the "bond-valence sum" (BVS) approach.[12] According to this approach, the effective valence of an ion in a crystal is estimated by summing over all nearest-neighbor cation-anion bond valences (BV). The latter have been estimated from an empirical relation $[\mathrm{BV}=\exp[(R_0-R)/B]]$ that includes the measured bond length (R) and two adjustable parameters (R_0 and B). These parameters, it is assumed, are identical to those obtained from numerous well known and perfectly ordered crystals, e.g., $B=0.37$ Å. R_0 has been tabulated according to the specific cation-anion pair, the coordination sphere, and the oxidation state. The success of this approach was well demonstrated in $YBa_2Cu_3O_{7-\delta}$, where the variation in the BVS of Cu(2) (plane copper) vs δ correlates very well with the variation of T_c vs δ.[6]

We have examined bond lengths and BVS in the present family, but could not identify any specific pattern in bond length or BVS vs x similar to the one observed in the dependence of T_c on x or on y. In particular, no variation similar to the double-plateau behavior of T_c vs x could be identified in any of the bond lengths or BVS. We conclude that in this system BVS and bond lengths are not directly related to T_c or even to charge distribution.

The BVS approach has been strongly criticized recently by Jansen and Block.[13] The main problem seems to be the application of this empirical approach, that is based on parameters derived from ordered crystals *in equilibrium,* to other systems where the bond length may be contracted or elongated ("disordered" systems) due to chemical (internal) or physical (external) pressure. Even though these authors provide a theoretical basis to the empirical approach, they specifically criticize the deduction of effective valence in YBCO (e.g., hole concentration in the planes) from these BVS under normal pressure, and particularly under high-pressure conditions. We believe that their criticism is correct: the interpretation of effective valence in a strained system such as YBCO is not justified. Recall that a deviation of only 1% in the actual Cu(2)—O bond length (i.e., $\Delta R \cong 0.02$ Å) from its ordinary value in other compounds yields ~5% deviation in the calculated bond valence due to the exponential dependence ($e^{0.02/0.37}=1.05$).

Notwithstanding, it is possible to conclude from the BVS approach that internal stresses exist when the calculated valence differs significantly from its ordinary value. For instance, we noticed that the calculated BVS of La_Y is remarkably large ($\sim +4$) while that of La_{Ba} is quite small ($\sim +1.5$) as compared to the ordinary oxidation state of La ($+3$). This result is in accord with the intuitive assumption that La_Y is compressed, i.e., R_0 is to be taken smaller (La_{Ba} is rarefied) due to the small (large) volume of the Y (Ba) site, respectively, as compared to the volume of the La ion.

C. Interlayer distance

An interesting attempt to correlate T_c with various properties of a 2D electron gas has been proposed recently by Harshman and Mills.[14] These authors show that for many layered superconducting materials, optimized with respect to stoichiometry and order, an inverse relationship of the form $T_c = 300/d$ holds, where T_c is measured in K and d in Å. d denotes the spacing between coupled layers, e.g., adjacent CuO_2 planes in HTSC. An optimal material within a given family would require, according to these authors, the highest attainable oxygen stoichiometry, fully ordered oxygen sublattice, and minimal disorder or chemical inhomogeneity of the cations.

In the present family not all members can be considered optimal, since the transition is broadening at low x. We note that in the $0.4 \leq x \leq 0.5$ range, T_c falls well on that line ($T_c d = 283$ K Å) indicating an optimal oxygen stoichiometry, while implying again that disorder due to Ca distribution, which could be maximal at $x = 0.5$, is of little importance. The largest deviation from this line (i.e., $T_c d \cong 172$ K Å) is observed for the $x = 0.0$ member having the lowest y. The 3% increase in Cu(2)-Cu(2) spacing with decreasing x is, by far, insufficient to account for the observed decrease in T_c that would require an increase in d by a factor of 2.

As was noted earlier, it is possible to raise y of the $x = 0$ member, thereby increasing T_c. Therefore, we are currently investigating the possibility of raising y in the low-x members, in an attempt to obtain optimal materials. The work of Harshman and Mills suggests that it would be possible to raise T_c in the low-x members.

D. Oxygen-ordered domains

Recently, Poulsen *et al.* have proposed a simple model for the variation of T_c with δ in $YBa_2Cu_3O_{7-\delta}$.[11] It is based on the assumption that a 2D domain having almost perfect oxygen order and minimal size (i.e., no more than one vacancy within the domain) has to exist in the plane of the chains, in order to support electron transfer from the planes to the chains. They propose that to each of the ortho-I ($T_c = 92$ K) and ortho-II ($T_c = 58$ K) phases, there corresponds a specific domain. The domains of both phases differ by their size (area) and by their oxygen arrangement. The number of these domains has been determined from the oxygen distribution in this plane. The latter has been obtained as a function of δ by Monte Carlo simulations of the actual oxygen distribution at a given δ, based on known pair interactions between an oxygen and its possible neighbors. The number of domains of each phase was then used to interpolate T_c between both plateaus. Based on the above assumptions, these authors were able to accurately reproduce the measured dependence of T_c vs δ.

It is difficult to see how this model could be applied to predict the variation of T_c vs x in the present family, since y is essentially constant. It would perhaps be possible to correlate changes in x, that is, in the La_{Ba} concentration, with different oxygen ordering since the pair interactions between oxygens would also depend on x.

V. CHARGE REDISTRIBUTION: THE EFFECT OF COSUBSTITUTION ON HOLE DENSITY

Our main observation, namely, that T_c increases and ρ decreases with increasing x immediately raises the following question: If the only effect of the addition of Ca_Y is merely full compensation by the addition of La_{Ba}, then no change in T_c or ρ is expected, since the hole density would not change. This is naively suggested by the countereffect of these electron acceptors and donors; in other words, the number of Ca_Y acceptors equals the number of La_{Ba} donors. As we have seen, however, there is a rather strong dependence of T_c and ρ on the

Ca_Y/La_{Ba} concentration.

Therefore, we assume that electrons contributed by substituting La_{Ba} (La that substitutes for Ba) are not fully compensating the electrons that have been captured by Ca_Y (Ca that substitutes for Y). Instead, for each Ca_Y, one electron goes from the CuO_2 planes to the nearby Ca, yielding an increment in hole density in these planes. At the same time, for each La_{Ba}, a *fraction* of the electrons goes to the plane of the CuO "chains," and the complementary fraction goes to the CuO_2 planes, thereby lowering the increment in hole density in these planes. The net effect of this cosubstitution is then an *additional* charge transfer from the planes to the chains: the holes that are generated by electron transfer from the CuO_2 planes to the Ca_Y, are *partly* compensated by electrons that transfer from the La_{Ba} to the CuO_2 planes. The additional number of holes that are contributed to the planes in this way equals the number of electrons that transfer from the La_{Ba} to the "chains." It is possible that the charge transfer from the La_{Ba} to the chains is enhanced in the present system due to oxygen accumulation in the vicinity of the La_{Ba}. The latter is consistent with the tetragonal structure.

We have referred to the charge transfer due to cosubstitution as "additional" since when there is no substitution (i.e., at $x=0$), T_c does not vanish. In other words, at $x=0$ [that is, in the material $La(Ba_{1.75}La_{0.25})Cu_3O_{7.01}$] ordinary charge transfer between planes and "chains" takes place. It is, however, unclear why T_c has dropped so much (to 47 K) compared to the similar material $LaBa_2Cu_3O_7$ which has $T_c=92$ K (Ref. 15): The addition of a 0.25 La atom per unit cell in the $x=0$ material, and the slight increase in y are equivalent to an increase of $\sim\frac{1}{4}$ electron/unit cell at the most. Usually it takes more electrons to reduce T_c by that much (e.g., as is well known in reduced $YBa_2Cu_3O_{7-\delta}$). This might suggest a narrowing in the density of states in the present family as compared to $LaBa_2Cu_3O_7$. According to the BCS theory, T_c is related to $N(E_F)$, the density of states at the Fermi energy (E_F). The effect of substituting La for Ba is not only to add $\sim\frac{1}{4}$ electron/unit cell thereby raising E_F. We suggest that, in addition, this chemical substitution also induces changes in band structure, e.g., narrowing of the density of states. Hence despite a relatively small change in electron density, $N(E_F)$ becomes substantially smaller than it would be in $LaBa_2Cu_3O_7$, and T_c decreases. Notice that $LaBa_2Cu_3O_7$ that does not contain La_{Ba} is orthorhombic. It is possible that La_{Ba}, through its affinity to oxygen, causes the changes in band structure. Thus the band narrowing might be specifically related to the La_{Ba} rather than to the La_Y.

In support of the existence of band narrowing already in the $x=0.0$ member, we mention that this composition is quite sensitive to changes in y. Recall that T_c increases by ~ 10 K upon increase in y by only 0.04 (Sec. III C). By comparison, the same increase in y will induce in YBCO an increase in T_c of ~ 5 K at the most. It would be interesting to investigate by other methods the possibility of band narrowing due to La substitution.

VI. CONCLUSIONS

(1) We have found that $CaLaBaCu_3O_y$ does not exist as a single phase under ordinary preparation conditions. Instead $(Ca_{0.5}La_{0.5})(Ba_{1.25}La_{0.75})Cu_3O_y$ is formed as a major phase, and the material contains impurity phases.

(2) We have prepared a family

$$(Ca_xLa_{1-x})(Ba_{1.75-x}La_{0.25+x})Cu_3O_y$$

belonging to the 1:2:3 system that is tetragonal throughout the single-phase existence range $0.0 \le x \le \sim 0.5$. Cosubstitution of Ca_Y and La_{Ba} is responsible for the constant charge ($Q=7.25$) of the noncopper cations.

(3) In this family T_c varies both with x and with y. The variation with x resembles the double-plateau behavior of T_c vs δ in $YBa_2Cu_3O_{7-\delta}$.

(4) At least half of the variation of T_c between both plateaus is due to the change in x, and would also occur at strictly constant y.

(5) We have examined several models including ordinary charge transfer between planes and "chains," bond-valence sums, and oxygen ordering in domains and found them insufficient to explain the variation of T_c with x.

(6) We propose that in systems with cosubstitutions, *additional* charge transfer from planes to "chains" is responsible for the variation of T_c with x. In particular, electron transfer from the planes to the Ca_Y is only partly compensated by electron transfer from the La_{Ba} to the planes, since another fraction of the electron goes from the La_{Ba} to the "chains."

(7) La_{Ba} seems to play an important role not only as a donor in this family; through its affinity to oxygen it also promotes the tetragonal structure, assists the electron transfer to the chains, and helps in increasing the oxygen stoichiometry. It is also possible that substitution of La for Ba induces significant changes in band structure.

ACKNOWLEDGMENTS

We would like to thank C. Kuper and A. Ron for helpful discussions. We also thank N. Arbel and Y. Balaban for technical assistance. The research was supported by the Technion V.P.R. Fund—Posnansky Research Fund in High Temperature Superconductivity.

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