PHYSICAL REVIEW B VOLUME 50, NUMBER 6 1 AUGUST 1994-II

Effect of pressure and quenching on superconductive $La_2CuO_{4+\delta}$ $(0<\delta<0.1)$

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(Received 22 June 1993; revised manuscript received 7 April 1994)

Samples of $La_2CuO_{4+\delta}$ in the range $0<\delta<0.1$ were prepared by electrochemical insertion of oxygen in KOH; the oxygen content was determined by iodometric titration. The temperature variations of resistance R and Seeback coefficient α were used to monitor as a function of the compositional parameter δ not only the evolution of the superconductive transition temperature T_c, but also the diffusion-controlled spinodal phase segregation occurring in the temperature range $200<T\leq 300$ K. The data also show that the δ interstitial oxygen atoms O_i per formula unit enter as O_i^{2-} ions at least in the range $0<\delta\leq 0.070$. Comparison of the transport properties of samples slow-cooled from room temperature to 77 K reveals an O_i-atom segregation over the range $0<\delta\leq 0.066$; this segregation disappears for $\delta>\delta_o$ where the O_i atoms become ordered, and $0.066<\delta_o<0.070$ was determined. Analysis of neutron-diffraction data from available literature gives a spinodal decomposition temperature T_s vs δ that falls to 200 K at $\delta_s(\max)\approx 0.05$; the diffusion-controlled spinodal phase segregation occurs within the phase field of the O_i-disordered orthorhombic structure. The oxygen-rich phase having $\delta_s(\max)\approx 0.05$ is superconductive with a zero-resistance temperature $T_0=26$ K that is lower than the $T_0=32$ K observed for $\delta>\delta_o$; T_0 falls to a minimum near $\delta=0.0625$ within the compositional range $\delta_s(\max)<\delta<\delta_o$, which suggests the presence of a competitive nonsuperconductive line phase near $p=\frac{1}{8}$ holes per Cu atom as is found in the $La_{2-x}Ba_xCuO_4$ system near $x=\frac{1}{8}$. A nonsuperconductive transition at $T_d=47\pm 1$ K was found in slow-cooled samples over the range $0<\delta<\delta_o$; it is suppressed by both high pressure and the quenching procedure. We associate it with the competitive nonsuperconductive phase stabilized near $p=\frac{1}{8}$. In the ordered-O_i phase found for $\delta>\delta_o$, a "tail" in the R-vs-T curve extends into the superconductive temperature range where $\alpha=0$; it is attributed to a liquid-vortex state rather than a second superconductive phase. The pressure dependences of T_c and the O_i-atom mobility were used to distinguish the superconductive phases found for $\delta<\delta_o$ and $\delta>\delta_o$. The appearance of a nonsuperconductive line phase in the interval $\delta_s(\max)<\delta<\delta_0$ permits reconciliation of the data, including indirect evidence for charge fluctuations stabilized below a $T_p<150$ K in this interval. The indirect evidence for charge fluctuations is the same as that discussed by us elsewhere in the framework of a model developed for the system $La_{2-x}Sr_xCuO_4$.

INTRODUCTION

As early as 1987, filamentary superconductivity was discovered in ceramic samples of La_2CuO_4 that had been slow cooled in air from the sintering temperature.[1,2] This procedure loads the structure with excess oxygen to yield $La_2CuO_{4+\delta}$ with a maximum $\delta\approx 0.02$.

In order to explore this phenomenon further, samples were loaded to higher values of δ with high oxygen pressures,[3-5] and a spinodal phase segregation into an oxygen-rich superconductive phase and an oxygen-poor antiferromagnetic phase was shown to occur below a temperature T_s.[6] Neutron-diffraction studies[6-8] performed on $\delta\approx 0.03$ samples prepared under a $P_{O_2}=3$ kbar have given a range $290\leq T_s\leq 320$ K for the onset temperature for phase segregation and a $T_t\approx 430$ K for the orthorhombic-tetragonal transition in the single-phase region. They also indicated that the oxygen-poor, antiferromagnetic phase that initially appears on cooling is essentially the parent compound La_2CuO_4; its concentration increases with decreasing temperature whereas the oxygen parameter δ_s of the superconductive phase increases with decreasing temperature. The phase segregation occurs via a diffusion of the oxygen atoms, and surprisingly these remain mobile down to about 200 K.[8,9]

Identification of the driving force for the observed segregation into a superconductive phase and the parent antiferromagnetic-insulator phase could prove critical to our understanding of the superconductive phase. Two alternatives need to be distinguished: (1) an electronic character of the normal state that makes the superconductive phase thermodynamically distinguishable from both the parent antiferromagnetic phase and the overdoped metallic phase and (2) an ordering of the interstitial oxygen in the superconductive phase. In order to distinguish between these alternatives, it is necessary to investigate systematically the compositional range $0.05<\delta<0.07$, a range that has been absent from previous studies. However, this range may be complicated by the appearance of a competitive, nonsuperconductive phase appearing near the composition $\delta=0.0625$, which corresponds to $p=\frac{1}{8}$ holes per Cu atom.

A thermodynamically distinguishable normal state

Whereas the $\delta=0.03$ samples retain their excess oxygen at atmospheric pressure to 489 K (Ref. 6), samples

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$\delta \approx 0.05$ prepared at higher P_{O_2} begin to lose oxygen above room temperature.[5] All samples with $\delta \geq 0.03$ exhibit a first-order phase change with loss of oxygen above 225 °C at atmospheric pressure.[5,7] For the $\delta \approx 0.05$ sample T_t is lowered to near room temperature, and a discontinuous increase in the room-temperature Cu-O bond length in the CuO_2 sheets was noted after traversing the first-order phase change with loss of oxygen near 225 °C; this increase in bond length was interpreted to indicate that a discontinuous increase in the equilibrium Cu-O bond length occurs on changing from a more covalent to an ionic character of the Cu-O bond.[5] A discontinuous change in bond character implies a double-well potential for the Cu-O bond at the crossover from ionic to covalent bonding. One consequence of such a double-well potential would be a stabilization by high pressure of the tetragonal relative to the orthorhombic phase, i.e., a $dT_t/dP < 0$[10], and this pressure dependence of T_t has been observed.[11] The orthorhombic-tetragonal distortion at a transition temperature T_t is due to a mismatch of the basal-plane La-O and Cu-O bond lengths in the tetragonal structure that makes the tolerance factor

$$t \equiv [\mathrm{La-O}]/[\sqrt{2}[\mathrm{Cu-O}]] < 1 \qquad (1)$$

decrease with decreasing temperature because of the larger thermal expansion of the La-O bond. A $t < 1$ places the Cu-O bonds in the CuO_2 sheets under a compressive force that is relieved by the distortion to the orthorhombic phase.[12] From Eq. (1), a $dT_t/dP < 0$ therefore signals a $dt/dP > 0$, which means that the Cu-O bonds in the basal plane are more compressible than the La-O bond as predicted for a double-well potential for the Cu-O bonds of the CuO_2 sheets, provided a large fraction of the longer, ionic Cu-O bonds are present in the sheets.

A double-well potential for the Cu-O bond not only has important implications for the character of the normal state of the superconductive phase;[13] it also provides a first-order driving force for a segregation in the range $0 < \delta < 0.05$ between a parent antiferromagnetic phase with all ionic bonding and a second phase with either all covalent bonding or a vibronic resonance between ionic and covalent bonding. Were the second phase a conventional metal, we could anticipate that in it all the Cu-O bonding would be covalent. However, stabilization of a high-T_c superconductive phase rather than a conventional metal has led us to postulate the existence of a vibronic resonance between the two types of Cu-O bonding with the formation of a correlation-polaron gas above room temperature that condenses below room temperature into a polaron liquid.[13] In this paper, we are interested only in the fact that, in a mixed-valent system, a double-well potential can provide a *vibronic* driving force for the observed phase segregation below room temperature in $La_2CuO_{4+\delta}$. We[14,15] have assumed such a driving force exists in our interpretation of the phase diagram for the system $La_{2-x}Sr_xCuO_4$.

Ordering of the interstitial oxygen

On the other hand, a conventional structural phase change could also provide the driving force for the phase segregation. The excess oxygen in $La_2CuO_{4+\delta}$ has been located by neutron diffraction;[8] it resides in the interstitial position between LaO planes that is coordinated by four La and four apical oxygen atoms. As first demonstrated[16] for $La_2NiO_{4+\delta}$, this position is partially occupied in oxygen-excess compounds having the K_2NiF_4 structure. Evidence for a structural phase change occurring in the interval $0.05 < \delta < 0.07$ comes from samples containing $\delta > 0.05$. Such samples have been prepared electrochemically by a method pioneered by Wattiaux *et al.*[17] A preliminary phase diagram below room temperature has been developed by Grenier *et al.*[18] This latter study showed a linear decrease with increasing δ in the room-temperature orthorhombicity of the structure for $\delta \leq 0.05$, which is consistent with a random distribution of the excess oxygen in the interstitial sites. The insertion of interstitial oxide ions not only expands the LaO-δO_i-LaO layers; it also relieves the compressive stress on the CuO_2 sheets by oxidizing them, so the tolerance factor t increases and T_t decreases with increasing δ. On the other hand, the structures for $\delta \geq 0.07$ show a linear increase with δ in the orthorhombicity of the room-temperature structure, which signals that the interstitial oxygen atoms are ordered where $\delta \geq 0.07$ is found. An increase in the orthorhombicity with δ is consistent with the addition of interstitial oxygen in the special positions of the ordered phase. This deduction has been confirmed by neutron-diffraction data, which show superstructure lines indicative of oxygen ordering in samples with $\delta \approx 0.08$ and 0.12.[19] Moreover, no evidence of phase segregation has been found above 10 K in samples $\delta > 0.07$,[19] which shows that the phase with ordered oxygen is stable. Therefore this phase could provide a driving force for the phase segregation observed in the range $0 < \delta < 0.05$.

The $p = \frac{1}{8}$ phase

In order to determine whether the driving force for the phase segregation below T_s observed for $0 < \delta < 0.05$ is vibronic in origin or is due to an ordering of the interstitial oxygen atoms, it is necessary to determine the limiting value δ_s for the spinodal phase segregation as well as the critical value δ_o above which the interstitial oxygen atoms are ordered. To date, the range of compositions $0.050 \leq \delta < 0.070$ in which δ_o falls has not been explored. Moreover, this compositional range contains the composition $\delta = 0.0625$, which corresponds to $p = \frac{1}{8}$ holes per Cu atom if the interstitial oxygen is present as O_i^{2-} ions. In the $La_{2-x}Ba_xCuO_4$ system, the superconductive phase is completely suppressed at $x = \frac{1}{8}$,[20] and below 950°C superconductive samples with $0.13 \leq x \leq 0.25$ in this system are reported[21] to phase segregate via La and Ba diffusion into two nonsuperconductive phases: an $x \approx \frac{1}{8}$ and an overdoped metallic phase. At these temperatures, no structural transition is associated with the phase segregation. A similar stabilization of a nonsuperconductive phase may occur at $\delta = 0.0625$ in the system $La_2CuO_{4+\delta}$. Such a phase could provide an *electronic* driving force for the phase segregation found in the range $0 < \delta < 0.05$.

Therefore it is also necessary to know both δ_s and δ_o relative to $\delta = 0.0625$.

Evidence from neutron diffraction of a $\delta_s \approx 0.05 < \delta_o$

Chaillout *et al.*[8] have performed a structural refinement on a single crystal with $\delta = 0.032$ to determine the extent of phase segregation at various temperatures down to 15 K. At 15 K, the compound was segregated into the parent phase ($\delta \approx 0$) and a superconductive phase with a calculated $\delta_s = 0.048$. Moreover, the structure of the $\delta = 0.048$ phase was found to be the same as the average orthorhombic structure in the range $0 < \delta \leq 0.05$ at room temperature; there was no evidence of ordering of the interstitial oxygen. These data indicate a $\delta_s(\max) \approx 0.050 < \delta_o$, which supports the conclusion that the spinodal phase segregation occurring in the temperature interval $200 < T < 320$ K for $0 < \delta < 0.05$ is not due to an ordering of the interstitial oxygen atoms. Moreover, these data indicate a $\delta_s(\max) < 0.0625$, which suggests that a *vibronic* driving force is responsible for the phase segregation rather than either an ordering of the interstitial oxygen atoms O_i or an electronic stabilization of a $p = \frac{1}{8}$ phase.

Motivation and strategy of this paper

Our principal motivation for this study was to investigate further the driving force for the static phase segregation occurring in the compositional range $0 < \delta < 0.05$ in the system $La_2CuO_{4+\delta}$. We also wished to explore for evidence of a $p = \frac{1}{8}$ phase in the hitherto unexplored compositional range $0.05 < \delta < 0.07$. We monitor the temperature range of any phase segregation that is occurring from the temperature dependences of the resistance and thermoelectric power. From the pressure dependence of T_c, we are able to distinguish whether the orthorhombic distortion is due to a cooperative tilting of the CuO_6 octahedra or an ordering of the interstitial oxygen atoms. By comparing the transport properties of slow-cooled samples with and without high pressure with those of samples quenched from room temperature to liquid nitrogen, we reinforce the use of transport data to monitor the diffusion-controlled phase segregation.

A related study has been reported by Ahrens *et al.*[22] for a single composition $\delta = 0.032$; these authors used magnetic susceptibility and La nuclear quadrupole resonance (NQR) to probe the phase segregation. They argued, as have we,[15] that T_c increases with the size of the segregated superconductive domains where the domain size is comparable to the magnetic penetration depth. They found a systematic increase of about 4 K in the bulk critical temperature T_c (the transition midpoint) with decreasing anneal temperature T_a in the range $200 < T < 300$ K. A maximum $T_c = 29.6$ K with a magnetic-susceptibility onset temperature $T_{\text{on}} = 34$ K was reported for $T_a = 200$ K.

To explain our use of the temperature dependences of the Seebeck coefficient α and the resistance R to monitor the temperature range over which phase segregation is occurring, we cite the data of Hundley *et al.*[23]; they have demonstrated that in single-crystal $La_2CuO_{4+\delta}$, $\delta = 0.032$, the in-plane resistivity ρ increases with decreasing temperature over the temperature range of spinodal phase segregation, and the in-plane thermoelectric power α decreases with decreasing temperature. We have noted similar changes in the resistance R and in α in polycrystalline samples of $La_2CuO_{4+\delta}$;[18] they provide a definition of the temperature interval over which the static spinodal phase segregation is occurring for different values of δ, and we use this criterion in this paper.

Another example where this signature in the transport properties occurs is found in $La_{1.875}Ba_{0.125}CuO_4$, where a low-temperature tetragonal (LTT) phase coexists with the orthorhombic phase in the temperature interval $35 < T < 60$ K;[20] in this case, static cooperative atomic displacements make visible to diffraction the two distinguishable phases, which probably contain different charge-carrier concentrations. In this case, also, the two-phase region is characterized by a $dR/dT < 0$ and a $d\alpha/dT > 0$.

Our final motivation for this study is the need to clarify the situation in the overdoped region $\delta > 0.07$. Samples with $\delta \geq 0.07$ prepared electrochemically have exhibited a step in T_c suggestive of the presence of two superconductive phases, one with a $T_c \approx 36$ K and another with a $T_c \approx 41$ K. It is possible that the $T_c \approx 36$ K corresponds to the maximum T_c to be associated with the phase containing disordered interstitial oxygen and a $T_c \approx 41$ K corresponds to a phase with completely ordered interstitial oxygen. Samples in the range $0.07 \leq \delta \leq 0.12$ may be phase segregating at room temperature into domains of ordered interstitial oxygen within a matrix of disordered interstitial oxygen. Such an interpretation has been implied by Johnston *et al.*[24] in their magnetic investigation of electrochemically prepared $La_2CuO_{4+\delta}$. Alternatively, the step could be a manifestation of vortex motion in the superconductive state just below T_c.

EXPERIMENTAL

Polycrystalline samples were prepared by reacting in air a stoichiometric mixture of the oxides at 1030–1100 °C for 1 week with intermittent grinding. The La_2O_3 powder was calcined at 980 °C immediately before weighing. Before the final sintering, the powder samples were ground in a milling machine to obtain a finer powder than is obtainable with regular grinding. Sintering just above the reaction temperature of 1050 °C gave a hard, dense pellet. The samples were then oxidized electrochemically at room temperature following the procedure of Wattiaux *et al.*[17] and Grenier *et al.*[18] The amount of excess oxygen inserted electrochemically was controlled by the polarization time; however, oxygen evolution is a competitive side reaction, and the final oxidation state was determined by iodometric titration to within an error of better than ±0.01 for δ. In our experiments we obtained an accuracy better than ±0.005. The relatively high oxygen mobility at room temperature ensures that homogeneity of the oxygen distribution is obtained at room temperature within a few days. However, for samples 0.047 and 0.066 we inserted the oxygen electrochemically at 360 K in order to obtain easier control over the oxygen content. We obtained a $\delta = 0.054$ sample at room temperature, but we found it difficult to vary δ by small steps at room temperature in the range $0.034 < \delta < 0.070$. At room temperature, the samples were electrochemically oxidized quickly in this region to $\delta = 0.070$, which appears to be close to the order-disorder boundary δ_o. The evolution of properties with δ was not influenced by the temperature at which the samples were prepared. All samples were single phase to x-ray diffraction after both sintering and electrochemical oxidation.

Magnetic susceptibility was measured with a superconducting quantum interference device (SQUID) magnetometer. Measurements of the Seebeck coefficient were carried out with a home-made apparatus in which the temperature gradient ΔT across the sample was carefully controlled. Resistance measurements were made with a four-probe, dc technique; the background potential in the voltage pickup leads was subtracted out. Electrical resistance measurements under nearly hydrostatic pressure were performed with a Be-Cu self-clamping device[25] containing a Teflon cell, a lead manometer, and a 1:1 mixture of *n*-pentane and isoamyl alcohol as a pressure-transmitting medium. Indium was first pressed onto the sample surface for electrical contact. Thin copper wire was then pressed into the indium contact with small pieces of indium foil. The sample temperature was measured with a silicon diode attached to a place near the Teflon cell. During a measuring run, the cooling rate was computer controlled to be less than 0.1 K/min.

RESULTS

Figure 1 shows the Meissner effect for typical samples from three regions of the $La_2CuO_{4+\delta}$ system. The curve for the $\delta = 0.034$ sample is similar to that previously reported[24] for $\delta = 0.032$; that for $\delta = 0.070$ has a larger Meissner fraction and a higher T_c. Johnston *et al.*[24] reported the same higher Meissner fraction, but a lower $T_c = 30$ K, whereas Grenier *et al.*[18] reported two values of T_c, one near 40 K and the other near 30 K. We observe a single transition at 40 K. We also find (see below) a jump of 10 K in T_c on crossing the composition δ_o, where $0.066 < \delta < 0.070$. The literature does not report data for a $\delta = 0.054$ sample.

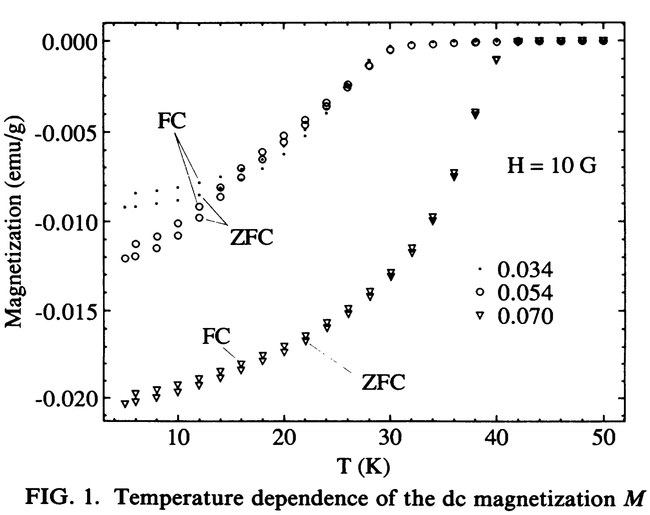

FIG. 1. Temperature dependence of the dc magnetization M in a field of 10 G for $\delta = 0.034$, 0.054, and 0.070.

The resistance versus temperature data for different hydrostatic pressures that are displayed in Figs. 2(a)–2(g) were highly reproducible. The high-pressure data were taken on samples that had been cooled slowly down to liquid-He temperatures. In order to clarify how a diffusion-controlled phase segregation occurring between 200 K and room temperature influences the low-temperature ($T < 50$ K) resistance data, measurements at atmospheric pressure were also carried out on all samples after quenching from room temperature to 77 K. Comparison of the resistance versus temperature curves for the same sample after a slow cool (0.2 K/min) and quenching is presented in the insets of Figs. 2(a)–2(g). Quenching was done by plunging the high-pressure chamber in liquid N_2, which lowers the temperature to below 200 K in about 1 min. The total cooling from room temperature to 77 K took about 5 min.

Table I provides information on several critical temperatures extracted from the data of Fig. 2. For samples with $0 < \delta < 0.070$, we distinguish two onset temperatures for a drop in the resistance with decreasing temperature in the range $T < 50$ K, a T_d and a T_{on} where $T_d > T_{\text{on}}$. The temperatures T_d and T_{on} in Table I correspond to the temperatures at which the slope of the R-vs-T curves of Fig. 2 abruptly increases on cooling. Hydrostatic pressure suppresses the resistivity drop at T_d; but for pressures $P < 10$ kbar, a $dT_d/dP < 0$ can be observed. On the other hand band, the onset temperature T_{on} for the superconductive transition increases with pressure and is not suppressed.

The critical temperature T_c in Table I is taken as the midpoint of the superconductive transition occurring below T_{on}. A $dT_c/dP > 0$ was observed for all samples $0.17 \leq \delta \leq 0.054$, but its magnitude decreased with increasing δ. A $dT_c/dP < 0$ was found for $\delta = 0.066$. The temperature for onset of zero resistance also had a pressure dependence $dT_0/dP > 0$ for $\delta = 0.017$ and 0.034; it vanished for $\delta = 0.054$. In contrast, samples with $\delta \geq 0.070$ had no T_d anomaly and a $dT_c/dP = dT_{\text{on}}/dP \approx 0.06$ K/kbar, a value lower than the 0.11 K/kbar found[10] for the orthorhombic superconductor $La_{1.85}Sr_{0.15}CuO_4$.

The increase in resistance with decreasing temperature in the range $200 < T < 300$ K observed at atmospheric pressure for slowly cooled samples correlates with the temperature domain where diffusion of the interstitial oxygen atoms has been shown to create a classic spinodal phase segregation. This feature is found in the R-vs-T curves of all samples $0.017 \leq \delta \leq 0.054$ slow cooled at atmospheric pressure, but it is not prominent in the $\delta = 0.047$ and 0.054 samples. Although this feature is not observed in sample 0.066 and is only weakly so in 0.047 and 0.054, the change in low-temperature resistance of these samples on quenching from room temperature to 77 K demonstrates that some oxygen movement occurs below room temperature in these samples also. We con-

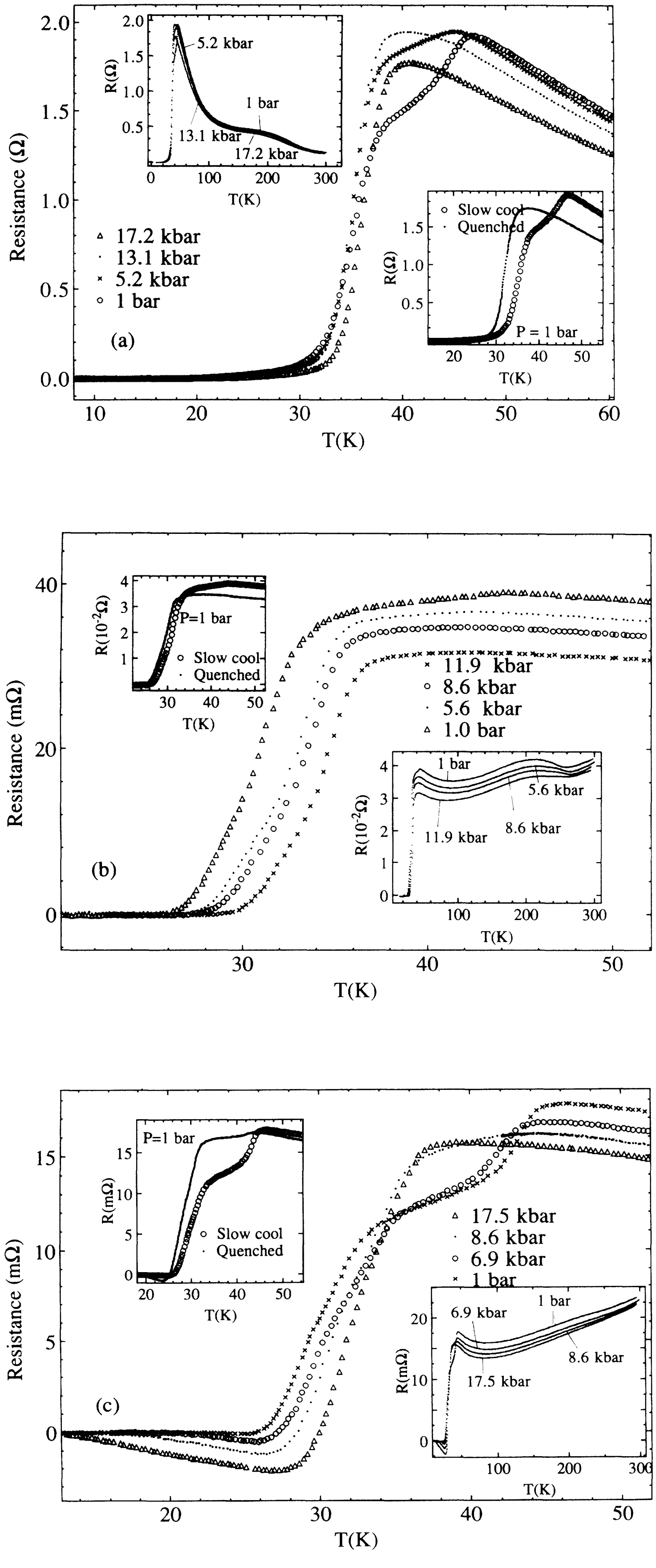

FIG. 2. Temperature and pressure dependence of the resistance for slow-cooled and (inset) quenched $La_2CuO_{4+\delta}$ with $\delta=$ (a) 0.017, (b) 0.034, (c) 0.047, (d) 0.054, (e) 0.066, (f) 0.070, and (g) 0.095.

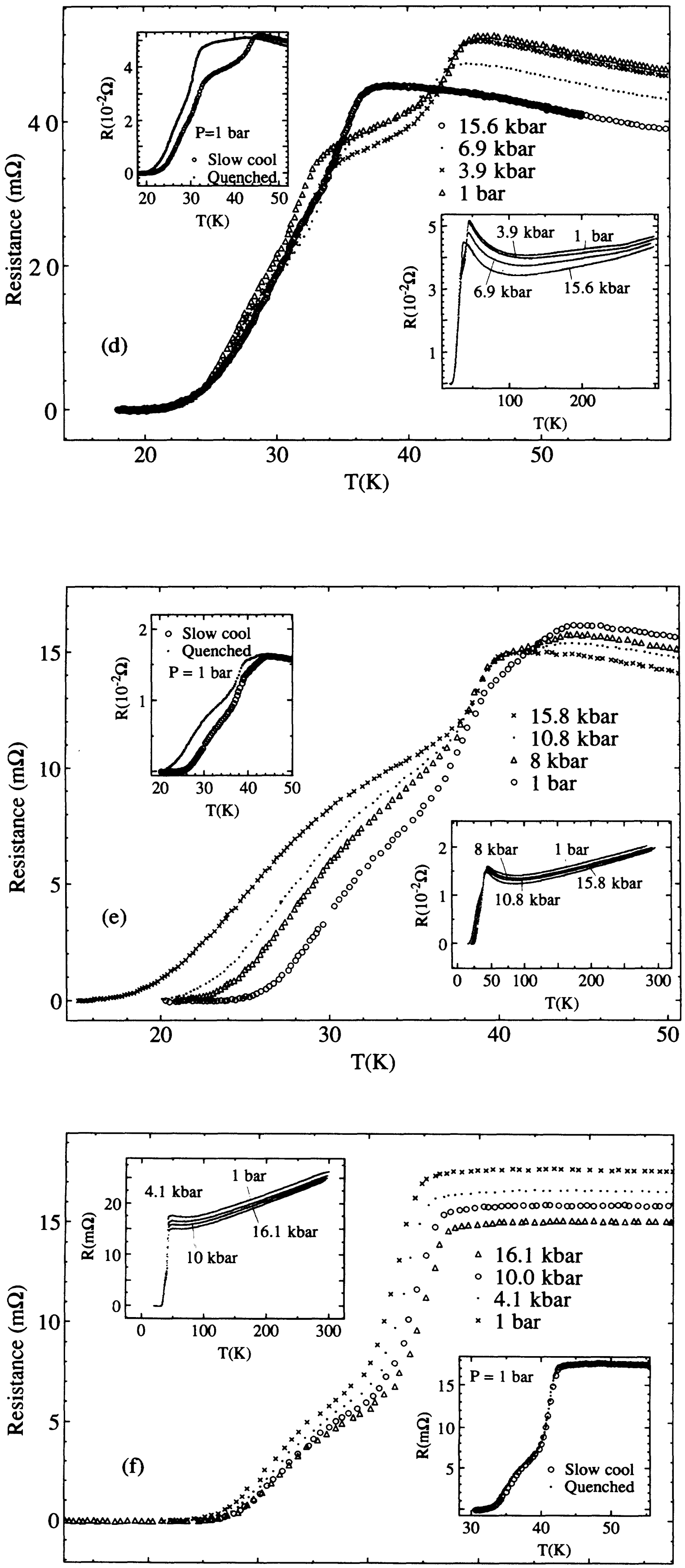

FIG. 2. (*Continued*).

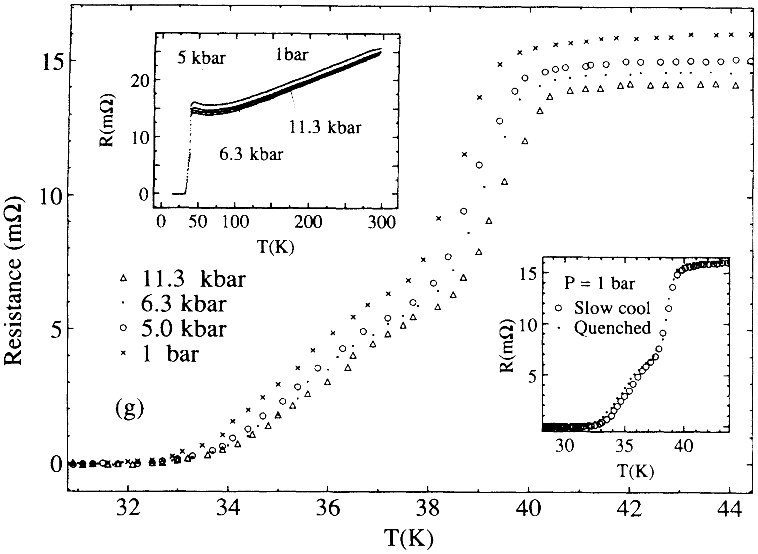

FIG. 2. (*Continued*).

clude from the quenching experiments that the interstitial oxygen atoms are mobile and induce phase segregation below room temperature in all samples investigated throughout the compositional range $0<\delta\le 0.066$, but for $\delta\ge 0.070$ the interstitial oxygen atoms do not move during cooling, as is confirmed by the absence of any difference in transport properties of the quenched and slow-cooled samples [see Figs 2(f) and 2(g)]. This observation tells us that the system is thermodynamically stable for $\delta\ge 0.070$ since the O_i atoms are still mobile at room temperature.

Figure 3 compares the temperature dependence of the Seebeck coefficient α and the resistance R for the $\delta=0.017$ and 0.070 samples; the former is representative of samples $\delta=0.017$ and 0.032, the latter of samples $\delta\ge 0.070$. A decrease in α and an increase in R with decreasing T are found for the $\delta=0.017$ sample in the range $200<T<300$ K where phase segregation is known to be occurring by oxygen diffusion. As mentioned above, this feature in α and R is characteristic of a temperature interval of phase segregation, not only in this system, but also in $La_{2-x}Ba_xCuO_4$; it is not found in the $\delta=0.070$ sample where there is no evidence of oxygen mobility. However, the $\delta=0.070$ sample exhibits a step in the resistance drop at T_c; this step is found in all samples $\delta\ge 0.070$ and is the same as that reported by Grenier *et al.*[18] The transition above this step is seen to increase with pressure; however, the R-vs-T curve is less sensitive to pressure for temperatures below this step, the temperature of essentially zero resistance changing little with pressure [see Figs. 2(f) and 2(g)].

Figure 4 compares the resistance drop with decreasing temperature at $T_d\approx 47$ K in the $\delta=0.054$ sample with the drop at $T_{\mathrm{on}}=43$ K in the $\delta=0.070$ sample. The thermopower voltage $V(T)$ is measured relative to a temperature of 50 K fixed on one side of the sample; the temperature T on the other side was controlled to scan the temperature region of interest. In Fig. 4, the Seebeck coefficient α was taken as the slope of the plot of thermopotential V versus T. The width of the resistivity and susceptibility transitions is somewhat broader than is found in the $La_{2-x}Sr_xCuO_4$ system, but it is similar to that found by others in the $La_2CuO_{4+\delta}$ system for the same values of δ.[18,24]

In the sample $\delta=0.054$, changes in $d\alpha/dT$ occur at both T_d and T_{on}, α falling to zero below T_0. A Meissner diamagnetism only sets in at temperatures $T<T_{\mathrm{on}}=35$ K, which is well separated from $T_d\approx 47$ K. No super-

TABLE I. Critical temperatures (see text for definition) versus composition for the system $La_2CuO_{4+\delta}$.

δ ± 0.005	T_d (K) ± 1 Slow cool	T_{on} (K) ± 1 Slow cool	T_c (K) ± 0.2 Quenched	T_c (K) ± 0.2 Slow cool	T_0 (K) ± 0.5 Slow cool	$\frac{dT_c}{dP}$ (K/kbar)
0.017	48	39	31.8	34.7	20	0.07±0.01
0.034	46	36	29.5	30.7	26	0.29±0.05
0.047	47	37	28.5	29.7	26	0.18±0.02
0.054	48	35	28.1	29.1	21	0.13±0.02
0.066	46	40	26.2	38.0[a] 29.2	24	−0.26±0.03
0.070		43.0±0.5	40.4	40.4	32	0.06±0.01
0.095		41.0±0.5	37.8	37.8	32	0.06±0.01

[a] Transition incomplete.

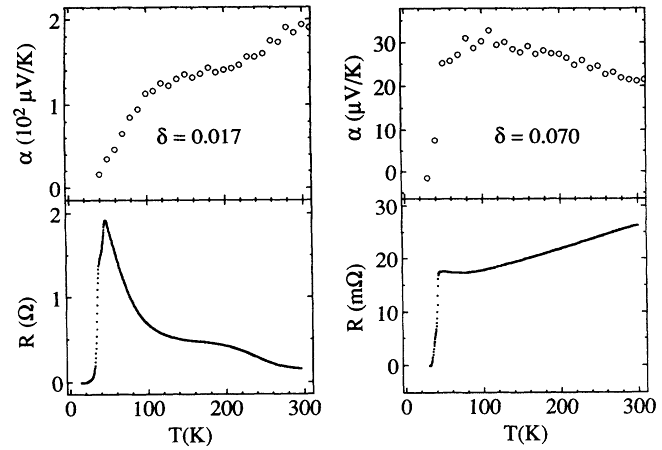

FIG. 3. Temperature dependence of the Seebeck coefficient α and the resistance R for $\delta=0.017$ and 0.070 in the system $La_2CuO_{4+\delta}$.

conductive transition is to be associated with T_d. The same is true for all samples $0.017\leq\delta\leq0.066$. In a magnetic field $H=0.1$ T, the magnetic susceptibility shows a small decrease setting in below T_d, but there is no Meissner diamagnetism.

In the sample $\delta=0.070$, on the other hand, the Seebeck coefficient drops to zero and a Meissner signal sets in below the first drop in resistance with decreasing temperature; it therefore marks an onset temperature $T_{\text{on}}=43$ K for superconductivity. However, an anomalous "tail" in the R-vs-T curve persists into the superconductive temperature range where $\alpha=0$. This "tail" gives rise to the step in R vs T at T_c discussed above in connection with Fig. 3. The presence of this step has suggested the existence of a second superconductive phase corresponding to $\delta=0.11$,[18,24] but an alternate interpretation is the prediction of Levi[26] that the high-T_c superconductors contain vortices in a liquid state to give a nonzero resistance even in the absence of an applied magnetic field. In our sample, the Meissner effect shows a single phase (Fig. 1), and we believe the latter interpretation applies in our case.

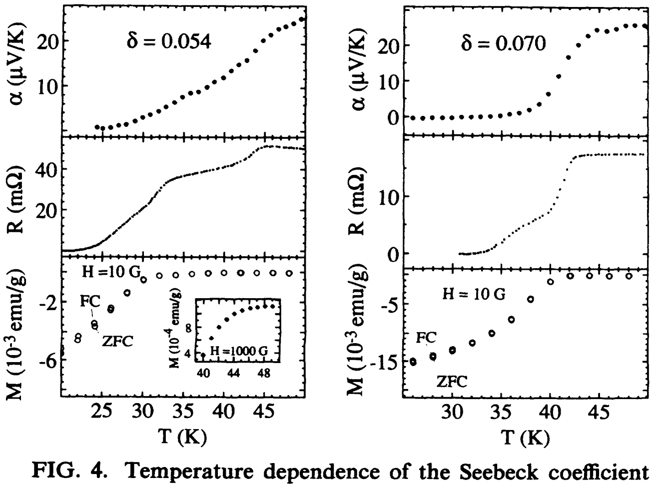

FIG. 4. Temperature dependence of the Seebeck coefficient α, the resistance R, and the dc magnetization M in a field of 10 G for $\delta=0.054$ and 0.070.

The feature characteristic of phase segregation appearing above 200 K in the R-vs-T curve for slow-cooled samples $0\leq\delta\leq0.054$ (with the exception of $\delta=0.047$ and 0.066) is increasingly suppressed by hydrostatic pressures (see Fig. 2). We conclude that hydrostatic pressure inhibits diffusion of the interstitial oxygen below room temperature.

An analogous increase in resistance with decreasing temperature occurs in all samples $0.017\leq\delta\leq0.066$ below 100 K; a decrease in α with decreasing temperature is also found in the same temperature interval. Unlike the similar feature in the range $200<T<300$ K, this feature occurring below 100 K in $La_2CuO_{4+\delta}$ is not suppressed either by quenching to 77 K from room temperature or by hydrostatic pressure; it is not associated with a diffusion-controlled phase segregation. A similar phenomenon is found in the $La_{2-x}Sr_xCuO_4$ system for $x\leq0.10$; we have interpreted it to signal the presence of charge fluctuations induced by cooperative, dynamic atomic displacements associated with a dynamic resonance between covalent and ionic equilibrium Cu-O bond lengths.[13] This feature is essentially absent in samples with $\delta\geq0.070$. The resistance deviates from a linear dependence only just above T_c in the samples $\delta\geq0.070$, the temperature dependence of the Seebeck coefficient α is totally different from that for $\delta=0.019$.

Finally, the sample with $\delta=0.047$, Fig. 2(c), exhibited a negative resistance just above T_0. The effect was highly reproducible for several different specimens cut from the same sample; it was found both after quenching under 1 bar and on the application of hydrostatic pressure, but was essentially absent in the sample slow cooled at atmospheric pressure. A very careful measurement of α vs T showed that $\alpha\neq0$ in the temperature range where the negative resistance occurs. Although pressure might cause the pressure-transmitting medium to become solid at low temperatures and to induce a shear stress on the sample, this explanation would not apply to the quenched sample; we rule it out. The four-probe configuration was not exactly the same as in the van der Pauw method. However, the origin of the negative resistance was not due to our experimental technique, but to something intrinsic to this sample. With the same experimental system, we have carried out extensive measurements on $La_{2-x}Sr_xCuO_4$ without encountering such an anomaly.[10] Normally, a fixed current establishes a distribution of equipotential lines in the sample that is invariant with temperature in a single-phase sample; only the voltage gradient changes. In this sample, the equipotential pattern must change with temperature just above T_0 so as to give rise to a crossing of the voltages at the two leads. A possible cause for such a crossing is the appearance of a phase inhomogeneity just above T_0 such as might be introduced by charge fluctuations.

DISCUSSIONS

T_s vs δ

The available data are summarized in the phase diagram of Fig. 5. We begin our discussion of it with the

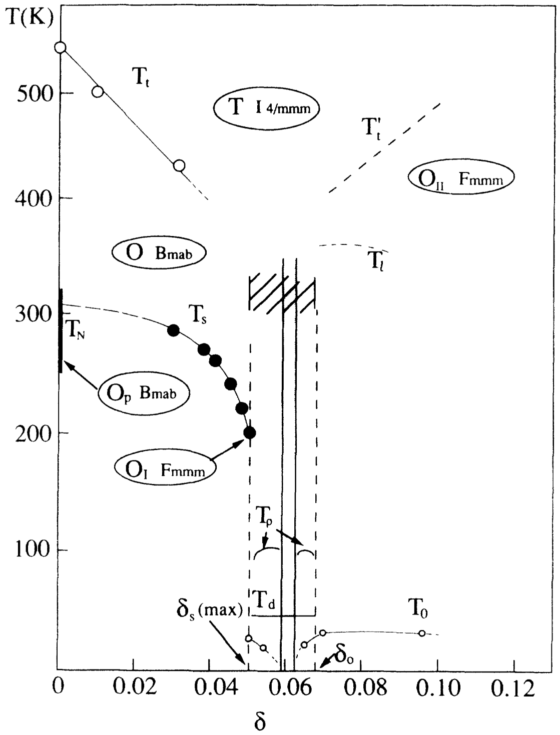

FIG. 5. Phase diagram for the system $La_2CuO_{4+\delta}$; δ_s(max)= maximum composition for spinodal phase segregation and δ_o = the O_i disorder-order composition. T_s and T_t lines were derived from data of Refs. 8 and 24. T_s: static spinodal phase segregation, T_N: Néel temperature, T_p: dynamic phase segregation (charge fluctuations), T_t: orthorhombic (*Bmab*) to tetragonal (*I4/mmm*) transition, T_t': orthorhombic (O_{II}*Fmmm*) to tegragonal (*I4/mmm*) transition, T_l: polaron liquid to correlation-polaron gas transition, T_0: zero-resistance temperature, T_d: transport anomaly associated with $p=\frac{1}{8}$ phase.

temperature T_s below which a diffusion-controlled phase segregation sets in.

The T_s for $\delta \approx 0.03$ has been reported to fall in the range $290 \leq T_s \leq 320$ K.[6-8] No detectable interstitial oxygen was found in the antiferromagnetic parent phase at low δ; the concentration of this parent phase increases with lowering temperature, but there is no evidence of a change in composition, which indicates a $\delta \approx 0$ for all temperatures $T < T_s$ in this phase. On the other hand, the evolution of lattice parameters with temperature[6-8] clearly indicates that the high-δ phase below T_s for $\delta = 0.03$ contains increasing concentrations of oxygen as the temperature is lowered to 200 K. Neutron-diffraction data from a $\delta = 0.032$ sample[6] show, for example, an abrupt change in the thermal-expansion coefficient at 200 K in the oxygen-rich phase, but no change in thermal expansion of the parent phase. The T_s-vs-δ points shown in Fig. 5 were calculated by us from the temperature variation of the fraction of parent phase reported in the literature.[8] A $dT_s/d\delta < 0$ is clearly indicated.

A recent publication[27] gives a somewhat different phase diagram than that shown in Fig. 5. It is based on neutron-diffraction data for a $\delta = 0.032$ sample that contradicts the earlier work.[6] The "lever rule" was used for three different compositions to locate a parent-phase boundary near $\delta = 0.01$ and a superconductive-phase boundary near $\delta = 0.055$. Within the titration error ± 0.005 for δ, the high-δ boundary is similar to ours. We apply the "lever rule" with the assumption that the limit of the parent phase is $\delta = 0$ on the earlier neutron-diffraction results.[6] We believe that Fig. 5 represents a more realistic phase diagram, but undoubtedly the parent phase has a finite, though small, limiting value of δ.

The superconductive phase at $\delta = \delta_s$

With $290 \leq T_s \leq 320$ K, some phase segregation occurs already at room temperature in samples with $\delta \approx 0.03$. Consequently Ahrens *et al.*[22] found that a $\delta = 0.032$ sample quenched from room temperature to 5 K was superconductive with a $T_c = 25.6$ K. Sufficient phase segregation had taken place at room temperature that the δ-rich phase at ambient conditions becomes superconductive. Since the δ-rich phase shows no evidence of an ordering of the interstitial oxygen, we conclude that the driving force for phase segregation is not structural; it is either vibronic or electronic. Since the δ-rich phase is superconductive, the driving force is not an electronic stabilization of a $p = \frac{1}{8}$ phase, which is not superconductive. The data are therefore consistent with a vibronic stabilization of a superconductive phase that, below 300 K, is thermodynamically distinguishable from the antiferromagnetic parent phase.[15,18]

Ahrens *et al.*[22] then annealed at temperatures $T_a \leq 250$ K the $\delta = 0.032$ sample that had been quenched into liquid He from room temperature. After each anneal, the sample was again quenched into liquid He. The superconductive critical temperature T_c increased as T was raised, reaching a maximum of 29.6 K for $T_a = 200$ K. The increase in T_c requires mobility of the O_i; the equilibrium distribution only occurs for $T \geq 200$ K. Over the range $200 \leq T_a \leq 250$ K, T_c decreased monotonically, extrapolating to 25.6 K for a room-temperature anneal. Since δ_s increases with decreasing T, these data indicate that the high-δ phase is underdoped with respect to the optimum oxidation of the CuO_2 sheets, which would account for an increase in T_c with δ_s in the δ-rich phase.

The Néel temperature

Whereas stoichiometric La_2CuO_4 has a $T_N \approx 320$ K,[28] the Néel temperature of the antiferromagnetic phase at the limiting composition of the parent compound remains at $T_N \approx 250$ K to $\delta \approx 0.03$.[24] The reduction in T_N from 320 to 250 K probably signals the presence of a $\delta > 0$ too small to be detected by neutron diffraction in the low-δ phase; it may also reflect internal strains associated with the coexistence of two phases created by diffusion below room temperature. We indicate in Fig. 5 a $\delta \approx 0$ for the parent phase, but $250 < T_N < 320$ K within this phase. For $\delta \geq 0.047$, we found no evidence for long-range magnetic order; any parent phase $\delta \approx 0$ has been reduced by $\delta = 0.047$ to too small a concentration to be detected at a $\delta \approx \delta_s$(max).

Location of $\delta \approx \delta_o$

For $\delta < \delta_o$, the orthorhombic distortion at lower temperatures is due to a cooperative rotation of the CuO_6 octahedra that relieves the internal stresses associated with bond-length mismatch. The orthorhombic-tetragonal transition temperature T_t decreases with increasing δ in the range $0 \leq \delta \leq 0.05$ because the tolerance factor t of Eq. (1) increases with δ where the interstitial oxygen atoms O_i are randomly distributed between pairs of LaO planes.[12,18] The O_i^{2-}ions relieve the tensile stress in the LaO-δO_iLaO layers, and oxidation of the CuO_2 sheets reduces the mean equilibrium Cu-O bond length.

An observed increase with δ in the room-temperature orthorhombicity for $\delta \geq 0.070$ is reflected in Fig. 5 by an undetermined (because of oxygen loss at $T > 300$ K) orthorhombic-tetragonal transition temperature T_t' increasing with δ. In this compositional range, the orthorhombic distortion is due to an ordering of the interstitial oxygen atoms; the CuO_2 planes remain flat in this orthorhombic phase.[19] A δ_o falling in the range $0.066 < \delta_o < 0.070$ is indicated by the disappearance of any evidence of phase segregation in samples $\delta \geq 0.070$. This deduction is also consistent with the dT_c/dP data of Table I, which are discussed below.

Oxidation state of the interstitial oxygen

The R-vs-T and α-vs-T curves of Fig. 3 for $\delta = 0.070$ are similar to those found for $x = 0.14$ in $La_{2-x}Sr_xCuO_4$; they are characteristic of an optimally doped copper oxide superconductor.[15] The similarity in magnitude of α and shape of α vs T for those samples indicates a hole concentration per Cu atom in each of $p = 0.14$, which would seem to confirm the hypothesis that below room temperature the interstitial oxygen is present as O_i^{2-} ions for $\delta = 0.070$.

A small, if any, change in T_c and the magnitude of α between $\delta = 0.070$ and $\delta = 0.090$ was previously interpreted[18] to mean that, for $\delta > 0.070$, the LaO-δO_i-LaO layers act as charge reservoirs because they have O-2p states that overlap the Fermi energy E_F. However, Table I indicates a definite decrease in T_c from 40.4 K for $\delta = 0.070$ to 37.8 K for $\delta = 0.095$. These values of T_c are compatible with the flat maximum in T_c vs x found in the range $0.14 \leq x \leq 0.19$ for $La_{2-x}Sr_xCuO_4$ where, without question, $p = x$ for a stoichiometric oxygen concentration O_4 per formula unit.[10] Therefore the data of Table I give no compelling reason to believe the interstitial oxygen enter as anything other than O_i^{2-} ions over the entire compositional range $\delta \geq 0.070$, particularly as $dT_c/dP \approx 0.065$ K/kbar for $\delta \geq 0.070$ is relatively small. Pressure generally alters the distribution of holes between a reservoir and the CuO_2 sheets so as to alter dT_c/dP significantly. On the other hand, $dT_c/dP = 0$ is found for flat CuO_2 planes in $La_{2-x}Sr_xCuO_4$,[10] and the large α does not decrease on increasing δ from 0.070 to 0.095 as would be expected for a large statistical contribution to the Seebeck coefficient; a $d\alpha/dx < 0$ occurs in $La_{2-x}Sr_xCuO_4$ on going from $x = 0.14$ to 0.18. The availability of a charge reservoir remains a distinct possibility for $\delta > 0.070$.

In the compositional range $\delta < 0.070$, the introduction of O_i atoms clearly oxidizes the CuO_2 sheets; it appears they enter as O_i^{2-} ions at lower concentrations. However, evidence for some charge transfer between the interstitial oxygen and the CuO_2 sheets can be found in the electronic behavior at T_d, a transition that we associate with the "$p = \frac{1}{8}$" phase. The Seebeck coefficient drops on lowering the temperature through T_d, which is consistent with a higher hole concentration in the CuO_2 sheets at temperatures $T < T_d$.

The layered structure of La_2CuO_4 supports strong internal electric fields associated with formal charges 2+ and 2− for the alternating $(LaO)_2$ and CuO_2 layers. These fields favor stabilization of O_i^{2-} ions within the rocksalt LaO-O_i-LaO layers; incorporation of O_i^{2-} ions lowers the formal charges of the layers to $(2-2\delta)+$ and $(2-2\delta)-$, which lowers the probability of electron capture by the O_i atoms as δ increases. Ordering of the interstitial oxygen at $\delta = 0.070$ apparently stabilizes electron capture at O_i^{2-} ions; in the disordered phase the transfer of electrons from the CuO_2 sheets to the O_i^{2-} ions appears to be less stable as δ increases. We attribute the peculiar experimental difficulty in obtaining electrochemically compositions in the range $0.035 < \delta < 0.070$ to this phenomenon.

Origin of the step at T_c for $\delta \geq 0.07$

Although we are unable to determine from our experiments whether the LaO-δO_i-LaO layers are acting as a charge reservoir in the range $\delta > 0.070$, nevertheless the step in the R-vs-T curve at T_c found in the range $\delta \geq 0.070$ can be attributed to liquid-state vortices rather than the presence of a second phase since the step gives an anomalous "tail" in the R-vs-T curve that extends into the superconductive temperature range where $\alpha = 0$.

The transition at T_l

Above a temperature T_l, where $300 \leq T_l < 500$ K, the system $La_{2-x}Sr_xCuO_4$ shows a complete solid solution over the entire compositional range $0 \leq x \leq 0.34$. The R-vs-T curve for $T > T_l$ changes gradually with increasing x from weakly concave to the temperature axis in the underdoped samples to a T^y dependence in the overdoped samples; y increases with x from $y = 1.0$ to $y \approx 1.4$ in the overdoped samples.[29] Below T_l, the α-vs-T and R-vs-T curve show a marked transition on passing from the underdoped compositions $0 < x \leq 0.10$ to the optimally doped compositions $0.14 \leq x \leq 0.20$. Whereas α is essentially temperature independent down to a $T_p \leq 150$ K in the underdoped samples, the characteristic feature of the α-vs-T curves for the optimally doped samples is a transition to a temperature dependence below T_l that exhibits a pronounced maximum, having a shape suggestive of the addition of a giant mass enhancement of the transport term. In these samples; R increases linearly with T below T_l. We have interpreted this behavior to be indicative of a *correlation-polaron gas* above T_l for all compositions $0<x<0.34$ that condenses below T_l into a *polaron liquid* having a stable compositional range $0.14 \leq x \leq 0.20$.[13] Since $p=x$ in the $La_{2-x}Sr_xCuO_4$ system for a stoichiometric oxygen content, we can expect the $La_2CuO_{4+\delta}$ system to exhibit the same α-vs-T and R-vs-T behavior in the range $0.07 \leq \delta \leq 0.11$ if the interstitial oxygen is present as O_i^{2-} ions. The curves for $\delta=0.070$ shown in Fig. 2 are similar to those for $x=0.14$ in $La_{2-x}Sr_xCuO_4$; however, they are restricted to $T<300$ K because of problems with loss of oxygen at higher temperatures. A possible change of slope in the α-vs-T curve at a $T_l \approx 300$ K is just discernible.

Indirect evidence for charge fluctuations in $La_2CuO_{4+\delta}$

According to the correlation-polaron model, underdoped samples in the range $0<p<0.10$ become metastable below 300 K with respect to a phase segregation into the parent and supeconductive phases. In $La_{2-x}Sr_xCuO_4$, conventional segregation into hole-rich and hole-poor domains is prevented by lack of a mobile ion; segregation only occurs below a $T_\rho \approx 150$ K via cooperative atomic displacements that, because of vibronic coupling, remain dynamic and therefore result in charge fluctuations.

A $\delta_s(\max) \approx 0.05$ at $T \leq 200$ K in Fig. 5 for $La_2CuO_{4+\delta}$ corresponds to a hole concentration per Cu in the CuO_2 sheets of $p \approx 0.10$ if all the O_i atoms are present as O_i^{2-} ions. A $p \approx 0.10$ still lies within the range of underdoped samples if optimum doping is restricted to $0.14 \leq p \leq 0.20$. It is therefore legitimate to ask why δ_s does not mark the boundary of optimum doping if the driving force for phase segregation is indeed stabilization of the superconductive phase. We answer that question qualitatively by noting that Coulombic repulsions between O_i^{2-} ions as well as the local lattice deformation around each O_i^{2-} ion resist stabilization of a higher-δ phase with disordered O_i^{2-} ions. This resistance accounts for a $dT_s/d\delta<0$ in Fig. 5. Were the O_i atoms mobile at $T<200$ K, a $\delta_s(\max)>0.05$ could be expected.

The signature for the onset of charge fluctuations below a $T_\rho \approx 150$ K in underdoped $La_{2-x}Sr_xCuO_4$ is a $dR/dT<0$ and a $d\alpha/dT>0$ in the range $T_c<T<T_\rho$, a behavior like that occurring in the interval $200<T<300$ K in $La_2CuO_{4+\delta}$ for $0<\delta<0.05$. The appearance of the characteristic signature $d\alpha/dT>0$ and $dR/dT<0$ below 100 K for all samples $0.017 \leq 0.066$, but not for $\delta \geq 0.070$, despite a static phase segregation to $\delta \approx 0$ and $\delta_s \leq 0.05$ in samples $0<\delta<0.05$, would therefore indicate that charge fluctuations persist in the interval $T_c<T<T_\rho$ for $0.050 \leq \delta < 0.070$. This conclusion appears surprising; however, the situation is made more complex by the insertion of a $\delta=0.0625$ phase, corresponding to $p=\frac{1}{8}$ lying within the range $0.10<p<0.14$. The insertion of this phase introduces the possibility of an electronically driven phase separation at low temperatures and also allows the evidence for a diffusion-controlled segregation via mobile O_i^{2-} ions in the $\delta=0.054$ and 0.066 samples to be reconciled with the T_s-vs-δ curve of Fig. 5 obtained from neutron-diffraction data.

The $p=\frac{1}{8}$ phase

With a $\delta_s(\max) \approx 0.05$ and a $0.066<\delta_o<0.070$, we need to ask what is happening in the range $\delta_s<\delta<\delta_o$. To answer this question, we monitor (a) the variation with δ of T_0, the temperature below which the resistance vanishes, (b) the evidence for a diffusion-controlled process occurring near room temperature in this compositional range, and (c) the temperature variation of R and α below 150 K that we have interpreted elsewhere to signal the onset of charge fluctuations.

From Table I, we see that the slow-cooled samples all have a $T_0=26$ K for $0<\delta<0.05$, which would indicate a common value of δ for the superconductive phase segregated out at $\delta_s(\max) \approx 0.05$. On the other hand, T_0 goes through a minimum in the interval $0.054<\delta<0.066$. This behavior is analogous to the suppression of T_c at $p=\frac{1}{8}$, corresponding to $\delta=0.0625$, that has been well established for the system $La_{2-x}Ba_xCuO_4$ at $x=p=\frac{1}{8}$. (A similar suppression of T_c may also occur near $x=\frac{1}{8}$ in a well-homogenized $La_{2-x}Sr_xCuO_4$ system.[30]) We are led to conclude that a similar nonsuperconductive phase is being stabilized near $\delta=0.0625$ in the $La_2CuO_{4+\delta}$ system and that stabilization of this phase is *electronically* driven. The transition at δ_o is *structurally* driven, and the phase segregation between the parent compound and the superconductive phase at $\delta_s(\max)$ has been postulated by us to be *vibronically* driven.

The $p=\frac{1}{8}$ phase may be stable above 300 K, as is demonstrated in $La_{1.84}Ba_{0.16}CuO_4$ by the phase segregation below 950 °C into two nonsuperconductive phases: one at $p=\frac{1}{8}$ and the other an overdoped metallic phase with $p>0.25$.[31] Evidence for a diffusion-controlled phase segregation in the $\delta=0.054$ and 0.066 samples would then be interpretable in the former as a phase segregation below T_l between a $p=\frac{1}{8}$ phase and a polaron-liquid superconductive phase at lower ($\delta \approx 0.05$) and, in the latter, between a $p=\frac{1}{8}$ phase and an O_i-ordered superconductive phase at higher ($\delta \approx 0.070$) values of δ.

Segregation of the $\delta=0.054$ sample into a superconductive $p \approx 0.10$ and a $p=\frac{1}{8}$ phase cannot be driven by the order-disorder transition of the interstitial oxygen since we found $0.066<\delta_o<0.070$. Moreover, only relatively small changes in the oxygen distribution are evident between the slow-cooled and the quenched samples or after cooling under pressure; the principal phase segregation appears to occur below T_ρ, which is consistent with an electronic stabilization of a nonsuperconductive $p=\frac{1}{8}$ phase that competes with a vibronically stabilized superconductive phase.

Effect of pressure

Hydrostatic pressure suppresses the resistive anomaly at $T_d \approx 47$ K that is found in all samples $0.017 \leq \delta \leq 0.066$, but not for $\delta \geq 0.070$. This transition is not superconductive. The drop in α with decreasing T at T_c begins at a $T_f \geq T_{\rm on}$ below which Cooper-pair fluctuations occur; the drop in α with decreasing T at T_d occurs at the temperature T_d of the resistive drop. No superconductive pair fluctuations are associated with T_d.

Pressure reduces the anomaly in the R-vs-T curves of Figs. 2(a)–2(d) in the range $200 < T < 300$ K, which indicates that pressure suppresses the O_i-atom diffusion. The suppression of T_d, but not T_ρ, with hydrostatic pressure shows that the anomaly at T_ρ is independent of O_i-atom diffusion whereas T_d may be associated with the diffusion-controlled phase segregation. In the $\delta=0.066$ sample, suppression of the O_i-atom diffusion by pressure results in a broadening of the superconductive transition over the interval 16–40 K. Since T_d is suppressed by quenching [see Fig. 2(a), for example], as well as by pressure, we are led to conclude that T_d is associated with the static component of the phase segregation to $p=\frac{1}{8}$.

We discuss the pressure effect on $T_c, dT_c/dP$ of Table I, within the context of the effect found for the system $La_{2-x}Sr_xCuO_4$ where a $dT_c/dP \approx 0.11$ K/kbar occurring in the orthorhombic phase at $x \approx 0.15$ becomes $dT_c/dP \approx 0$ in the tetragonal phase.[10] In the tetragonal phase, the Cu-O-Cu bond angle in the CuO_2 sheets is 180°; in the orthorhombic phase, a cooperative tilting of the CuO_6 octahedra reduces this angle, so we associate a $dT_c/dP > 0$ in $La_{2-x}Sr_xCuO_4$ with the deformation of the CuO_2 sheets by octahedral-site tilting. In $La_2CuO_{4+\delta}$, there are two distinguishable orthorhombic phases denoted $O_{\rm I}$ and $O_{\rm II}$ in Fig. 5. In the $O_{\rm I}$ phase, the O_i atoms are disordered and at 15 K the CuO_6 octahedra are tilted as in the orthorhombic phase of the system $La_{2-x}Sr_xCuO_4$; in the $O_{\rm II}$ phase the O_i atoms are ordered and at 4 K the CuO_6 octahedra are not tilted.[19] Therefore, in the absence of charge transfer between the CuO_2 sheets and a charge reservoir in the nonsuperconductive layers, the value of dT_c/dP can distinguish between an $O_{\rm I}$ and an $O_{\rm II}$ orthorhombic phase.

The application of pressure at room temperature inhibits, but does not suppress totally, further phase segregation below room temperature (see Fig. 1) in the range $0 < \delta < 0.05$. The decrease in dT_c/dP from 0.29 K/kbar for $\delta=0.34$ to 0.13 K/kbar for $\delta=0.054$ is consistent with an increase with δ in the Cu-O-Cu bond angle within the CuO_2 sheets to a value similar to that found for $La_{1.85}Sr_{0.15}CuO_4$. The low value $dT_c/dP=0.073$ K/kbar found for $\delta=0.017$ would then be consistent with the increase in T_c relative to T_0 in this sample as a result of internal stresses in the sample. In the $O_{\rm II}$ phase found for $\delta \geq 0.07$, where the Cu-O-Cu bond angles are 180°, a $dT_c/dP \neq 0$ may reflect charge transfer between La-δO_i-LaO charge-reservoir layers and the CuO_2 sheets. This latter question remains open, especially as hydrostatic pressure has essentially no effect on T_0 for $\delta \geq 0.07$. A $dT_c/dP < 0$ for $\delta=0.066$ is consistent with an inhibition of the static component of the segregation between the $p \approx \frac{1}{8}$ and superconductive $\delta \approx 0.07$ phases in this sample.

Finally, the origin of the negative resistance observed just above T_0 in the $\delta=0.047$ sample after quenching or under pressure remains unresolved. We simply note here that $\delta=0.047$ is at the upper boundary $\delta_s \approx 0.05$ for diffusion-controlled phase segregation.

CONCLUSIONS

From the experiments reported in this paper, we draw the following conclusions.

(1) In the system $La_2CuO_{4+\delta}$, the δ interstitial oxygen atoms O_i per formula unit enter the La_2CuO_4 host structure as O_i^{2-} ions for smaller values of δ, but in the range $0.054 \leq \delta \leq 0.066$ there may be some electron transfer from the O_i^{2-} ions to the LaO_2 sheets above a transition temperature T_d within a "$p=\frac{1}{8}$" phase. The extraordinary mobility (mobile down to 200 K) of the interstitial oxygen atoms suggests that the charge-transfer reaction

$$\delta O_i^{2-} + (CuO_2)^{(2-2\delta)-} = \delta O_i^{-} + (CuO_2)^{(2-\delta)-} \quad (2)$$

is not biased too strongly to the left, which allows oxygen diffusion to a neighboring site to be facilitated by an in-transit charge transfer. Ordering of the O_i at $\delta=0.070$ appears to stabilize the left-hand side of reaction (2) relative to the right-hand side.

(2) An order-disorder transition of the O_i atoms occurs at a composition δ_o, where $0.066 < \delta_o < 0.070$. The ordered phase has a T_c some 10 K higher than the disordered phase.

In the ordered phase, some O $2p$ states of the nonsuperconductive LaO-δO_i-LaO layers may lie above E_F to make these layers act as "charge-reservoirs" vis à vis the CuO_2 planes via the charge-transfer reaction of Eq. (2); but the small value of dT_c/dP for $\delta \geq 0.070$ suggests that any such charge transfer remains relatively small.

(3) In samples $\delta \geq 0.070$, the "tail" in the R-vs-T curve extending below T_c, as determined by $\alpha=0$, is to be attributed to liquid-state vortices.

(4) Below a critical temperature $T_s = T_s(\delta)$, where $dT_s/d\delta < 0$, a diffusion-controlled phase segregation occurs in the temperature range 200 K $< T < T_s$ where the O_i atoms are mobile. For a fixed δ, the fraction of parent phase with $\delta \approx 0$ and $T_N \approx 250$ K (reduced from a maximum $T_N \approx 320$ K in La_2CuO_4) grows with decreasing temperature as the oxygen content δ_s of the δ-rich phases increases to $\delta_s(\max) \approx 0.05$ at $T_s \approx 200$ K.

(5) A $\delta_o > \delta_s(\max)$ shows that the driving force for the phase segregation in the range $0 < \delta < 0.05$ is not stabilization of a phase with ordered interstitial oxygen; the driving force is not structural, but of electronic or vibronic origin. The electronic normal state of the superconductive phase is thermodynamically distinguishable from the antiferromagnetic state of the parent phase.

(6) A competitive phase, distinguishable from the two superconductive phases stable at $\delta \approx 0.05$ and $\delta \geq 0.070$, is stable within the narrow compositional range $0.054 < \delta < 0.066$, which lies in the domain of the disordered $O_{\rm I}$ structural phase field. The decrease in T_c to a minimum value within this narrow compositional range indicates that the competitive phase is most probably the nonsuperconductive $p=\frac{1}{8}$ phase, which would appear as

a line phase at $\delta \approx 0.0625$.

(7) A subtle transition appearing at $T_d \approx 47$ K over the range $0 < \delta < 0.070$ is nonsuperconductive and is suppressed by the application of hydrostatic pressure. This transition appears to be associated with the nonsuperconductive $(p = \frac{1}{8})$ competitive phase; it may represent a charge-transfer transition between the O_i^{-}/O_i^{2-} redox couple and the CuO_2 planes.

(8) It is possible to monitor known phase segregations by observing changes in the temperature dependences of the resistance R and the Seebeck coefficient α. Such monitoring showed that application of hydrostatic pressure suppresses the mobility of the O_i atoms. It also revealed an O_i-diffusion phase segregation occurring near room temperature in the narrow compositional range $0.054 \leq \delta \leq 0.066$. The latter finding is consistent with a competitive line phase near $\delta = 0.0625$ that is stable to above room temperature; segregation between it and the $\delta = 0.05$ superconductive phase would then occur below T_l for $0.05 < \delta < 0.0625$ and between it and the superconductive O_{II} phase at δ_o for $0.0625 < \delta < \delta_o$.

(9) The temperature dependences of R and α below 150 K show anomalies consistent with the appearance of charge fluctuations in the interval $T_c < T < T_p$. We interpret this indirect evidence for the onset of charge fluctuations as a further manifestation of the influence of an electronically stabilized competitive $(p = \frac{1}{8})$ phase.

(10) The evolutions with δ and T of R and α in $La_2CuO_{4+\delta}$ are consistent with their evolutions with x and T in the system $La_{2-x}Sr_xCuO_4$ if provision is made for the diffusion-controlled phase segregations occurring in the range $T > 200$ K.

The indirect evidence for charge fluctuations in the range $T_c < T < T_p$ for $0 < \delta < \delta_o$ supports our earlier model[13] that the uniqueness of the normal state of the superconductive phase is the condensation of a correlation-polaron gas into a polaron liquid.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of the Robert A. Welch Foundation, Houston, TX, the Texas Advanced Research Program, and the National Science Foundation.

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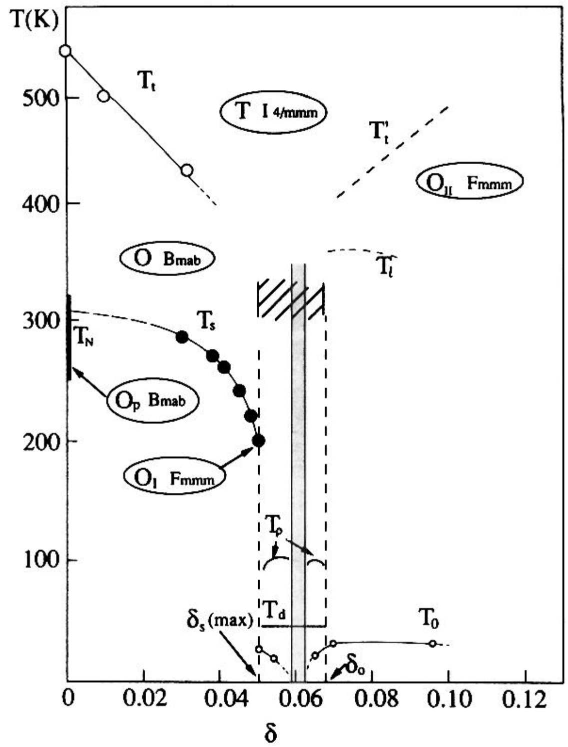

FIG. 5. Phase diagram for the system $La_2CuO_{4+\delta}$; $\delta_s(\max)$= maximum composition for spinodal phase segregation and δ_o = the O_i disorder-order composition. T_s and T_t lines were derived from data of Refs. 8 and 24. T_s: static spinodal phase segregation, T_N: Néel temperature, T_ρ: dynamic phase segregation (charge fluctuations), T_t: orthorhombic (*Bmab*) to tetragonal ($I4/mmm$) transition, T'_t: orthorhombic ($O_{II}Fmmm$) to tegragonal ($I4/mmm$) transition, T_l: polaron liquid to correlation-polaron gas transition, T_0: zero-resistance temperature, T_d: transport anomaly associated with $p=\frac{1}{8}$ phase.