Intrinsic tendency of electronic phase separation into two superconducting states in $La_{2-x}Sr_xCuO_{4+\delta}$

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The effect of hydrostatic pressure up to 2 GPa on the superconductiong transitions in $La_{2-x}Sr_xCuO_{4+\delta}$ is investigated. The ambient- and high-pressure properties of two series of samples with $x=0$ and 0.015 and $0 < \delta < 0.1$ are characterized and compared by ac-susceptibility measurements. At ambient pressure both sets of samples fit into the same phase diagram as a function of the total hole concentration n_h. For $n_h < 0.085$ there is a single superconducting transition ($T_c \approx 30$ K) with an unusually large pressure coefficient, $dT_c^{(30)}/dp \approx 10$ K/GPa. At a higher hole density ($n_h > 0.085$) a second superconducting transition ($T_c \approx 15$ K) follows the first transition upon cooling and the pressure shift of this transition is negative, $dT_c^{(15)}/dp \approx -4$ K/GPa. At the boundary as the hole density is close to 0.085 the phase separation can be induced by pressure. The results are explained in terms of a strong correlation of the interstitial oxygen with the hole system in the CuO planes. Pressure, applied at ambient temperature, causes a redistribution of holes. The mobile oxygen dopants follow and enhance T_c as well as the tendency toward phase separation. If pressure is changed at low temperature (< 100 K) the effects on T_c and phase separations are greatly diminished because the interstitial oxygen becomes immobile at low T. Our results indicate that the dopant effects are important. Dopants and holes should be treated as a single globally correlated state. When thermodynamic euqilibrium is approached in the oxygen-doped samples, we find that there is an intrinsic tendency of electronic phase separation of doped holes into two distinct superconducting states.

I. INTRODUCTION

Superconductivity in all high-T_c cuprates is induced by carrier doping. Except for the most recent results on field-doping experiments,[1] the vast majority of data available in the literature are based on chemical doping. Unfortunately, carrier doping by chemical substitution or intercalation is always accompanied by the introduction of dopants into the material, and the higher carrier concentration requires more dopants that inevitably affect the electronic state of the system. Even without any external perturbations, intrinsic dopant effects can-not be ignored. Furthermore, since carriers can be introduced either by cation and/or by anion doping, complications such as different lattice responses to accommodate different kinds of dopants have to be taken into account. Cationic doping proceeds via substitution of cations with ions of different valencies. We will use the notation "hard doping" since the cationic dopants occupy lattice sites and are immobile. Anionic doping, however, frequently results in a system of mobile dopants (e.g., interstitial or chain oxygen) that provides an additional degree of freedom and may respond to a change of thermodynamic parameters such as temperature or pressure. We will denote doping with mobile anions as "soft doping." $La_{2-x}Sr_xCuO_{4+\delta}$ is one of the high-T_c compounds that allow us to continuously tune the relative strength of "hard dopant" versus "soft dopant" of randomly distributed but immobile Sr ions (concentration x) and mobile interstitial oxygen ions (concentration δ), respectively. Accordingly, we can study their influences on the normal and superconducting states as a function of the hole concentration n_h, controlled by two parameters x and δ. We

use the notations "soft dopant" and "hard dopant" here instead of "annealed disorder" and "quenched disorder" to emphasize both the intrinsic nature (e.g., the dopant increases with increasing carrier density) and the strong coupling between carriers and dopants. The crucial parameter is the excess-oxygen doping. The high mobility of the interstitial oxygen provides not only the opportunity to study the "intrinsic" electronic evolution as a function of carrier concentration but also a number of interesting physical phenomena. For example, several structural transitions as well as macroscopic phase separations have been observed in $La_2CuO_{4+\delta}$ with increasing oxygen content.[2–9] For $0.006 < \delta < 0.05$ a miscibility gap was observed with two different structures (*Bmab* and *Fmmm* symmetry) coexisting at low temperatures. Chemically, the two structures show different oxygen contents. The *Bmab* structure is not superconducting, and its composition is close to stoichiometric La_2CuO_4, whereas the oxygen-rich *Fmmm* phase becomes superconducting at about 30 K.[2,3,5,6,8,9] The origin of this phase separation was attributed to the mobile interstitial oxygen since it is not found in the cation-doped $La_{2-x}Sr_xCuO_4$ where the dopants are immobile and "frozen" in their position. For $La_2CuO_{4+\delta}$, one superconducting transition was observed in the miscibility gap with $T_c \approx 30$ K, almost independent of δ.[2] At higher doping levels only one crystalline structure (*Fmmm*) was detected,[2,10] but evidence of the formation of superstructures by the interstitial oxygen was also reported.[4,10,12] Oxygen orderings along the c axis (staging)[12] as well as in the ab plane[4,11] were consequently proposed. It is interesting to note that the superconducting transition in this regime of the phase diagram (i.e., for $\delta > 0.05$) proceeds

in two well-defined steps at 30 and 15 K with no corresponding evolution of two chemical phases, suggesting the possibility of an electronic phase separation into two distinct superconducting phases.[2]

Different physical and chemical methods of superoxygenation of $La_2CuO_{4+\delta}$ have been employed. Originally high-pressure oxygen annealing was used to increase the O content up to $\delta=0.03$ in $La_2CuO_{4+\delta}$.[5,7] However, electrochemical intercalation of oxygen has been proven to be superior to all other methods of oxidization[10,13,14] because of the low reaction temperature (close to room temperature), the higher oxygenation level (δ) that can be achieved, and the precise measurement and control of the doping level. We have carefully studied various electrochemical techniques, and shown that samples so prepared are close to thermodynamic equilibrium for $0<\delta<0.05$ with a superconducting transition at $T_c\approx30$ K as long as the intercalation rate was low. High intercalation rates, in particular for $\delta>0.05$, resulted in nonequilibrium samples with T_c up to 45 K.[13,14] However, slow electrochemical oxidation followed by thermal annealing at 110 °C allows the samples to relax close to equilibrium, and T_c decreases to about 30 K. Outside the miscibility gap for $\delta>0.05$ a second superconducting transition with $T_c\approx15$ K develops with annealing, resulting in the two-step transition described in the previous paragraph.[2,14]

The appearance of different phases with increasing oxygen content is obviously related to the interstitial mobile oxygen ions, and cannot be observed in the cation-doped $La_{2-x}Sr_xCuO_4$. The strong correlation of the negatively charged O^{2-} ions with the hole carriers in the Cu-O planes is expected to result in a cooperative behavior and in interesting features like chemical and electronic phase separation, oxygen ordering, etc. reported in recent works. However, the driving force and the microscopic mechanism for these phenomena are still a matter of discussion. Based on a theoretical study of the phase diagram of a two-dimensional t-J model including the nearest-neighbor Coulomb repulsion Emery *et al.*[15,16] suggested that electronic phase separation into hole rich and hole poor phases may be a general property of two dimensional hole-like systems. In this case, the mobile oxygen in $La_2CuO_{4+\delta}$ plays an essential role by compensating for the repulsion between holes in the hole-rich regions and facilitating the charge separation. On the other hand, there is the possibility that the oxygen ions cause the separation into different (oxygen-rich and -poor) phases affecting the local hole density in the Cu-O planes. To separate and to distinguish between these two scenarios the hole density n_h and the oxygen content δ ought to be controlled independently. This major goal can be achieved by cation/anion co-doping in the system $La_{2-x}Sr_xCuO_{4+\delta}$. Starting with a fixed Sr content x in the parent compound, and tuning the oxygen doping δ, by electrochemical intercalation, the degree of cation and anion doping can be varied at will and the hole concentration can be controlled precisely. In order to compare samples with the same hole concentrations but different oxygen contents, the doping efficiency of Sr and O has to be known. We have calibrated the doping efficiency of pure oxygen and oxygen/strontium codoped samples. Whereas each Sr ion adds one hole, the doping efficiency of

oxygen has been shown to change with the hole density.[17] Below $n_h=0.06$ each oxygen ion dopes exactly two holes into the planes as is expected from the formal valency O^{2-}. However, for $n_h>0.06$ the doping efficiency of the oxygen decreases to 1.3 holes per O ion. Hall measurements have shown that for $n_h>0.06$ the additional holes partially occupy localized states and do not increase the Hall number.[18] For the Sr codoped compound the oxygen doping efficiency reduces from 2 to 1.3 at exactly the same critical hole density $n_h=0.06$, indicating that the O doping efficiency is controlled by the total hole density, i.e., by the electronic state. Therefore, the total hole density in $La_{2-x}Sr_xCuO_{4+\delta}$ is determined by $n_h=x+2\delta$ ($n_h<0.06$) and $n_h=0.019+1.3(\delta+x/2)$ ($n_h>0.06$), respectively.[17]

Pressure is known to increase T_c in most of the underdoped high-T_c materials. In $YBa_2Cu_3O_{7-\delta}$ it was found that the increase of T_c with pressure is enhanced by a pressure-induced ordering of the oxygen ions occupying the incompletely filled chain sites.[19–21] This effect is particularly large in the far underdoped region. Another compound where pressure (applied at ambient temperature) changes the oxygen configuration with a crucial impact on the superconducting properties is overdoped $Tl_2Ba_2CuO_{6+\delta}$.[22,23] Whereas in the two former compounds pressure is assumed to affect the hole density in the active CuO layer by transferring charges between the charge reservoir block and the CuO planes this mechanism does not apply to the La-214 high-T_c compound. In fact, from Hall measurements at high pressures it was concluded that the average carrier density in $La_2CuO_{4+\delta}$ does not change with the application of pressure.[18,24] The pressure effect on superoxygenated $La_2CuO_{4+\delta}$ has previously been studied with inconsistent pressure coefficients of T_c for various samples prepared and doped by high-pressure oxygen annealing as well as electrochemical intercalation.[25] We believe that early results were plagued by the problem of nonequilibrium samples.

Therefore, we conducted a careful investigation of the effect of hydrostatic pressure on the T_c and superconducting states of the strontium and oxygen codoped La-214 system, $La_{2-x}Sr_xCuO_{4+\delta}$. The goal of this work is twofold: (i) Phase separation in the correlated hole-oxygen system was already reported under ambient conditions.[2] The effect of pressure on the superconducting state and the phase diagram as a function of hole concentration is of primary interest. To probe the underlying driving mechanism of phase separation, the pressure is changed at ambient as well as at low temperatures (where oxygen motion is inhibited). (ii) The pressure effect on samples with different oxygen content δ, but the same hole density n_h, are compared to extract the most relevant parameter determining the nature of the superconducting state. Pressure is used as a tool to characterize the electronic state at a given n_h. We find that samples, both under ambient and high pressures, with different δ and x behave very similarly if compared at the same hole concentration. This indicates that the observed phase separation, although supported by the mobile oxygen ions, is primarily of electronic nature.

II. EXPERIMENTAL SETUP

$La_{2-x}Sr_xCuO_4$ was prepared by a standard solid-state reaction from oxides, and subsequently oxidized by electrochemical intercalation as described elsewhere.[2,14,18] After the electrochemical oxidization all samples were annealed at $110\,°C$ in oxygen for a period of 24 to 200 h. Samples with different Sr content, $x=0$ and 0.015, and excess oxygen $0 < \delta < 0.1$ were prepared and investigated at ambient and high pressure. dc magnetic susceptibility measurements using a Quantum Design SQUID (Superconducting quantum interference device) were employed to characterize the superconducting transition at ambient pressure. For the high-pressure experiments the ac susceptibility technique was used. A dual-coil system was mounted to the ceramic samples and the highly sensitive low-frequency (19 Hz) LR 700 (Linear Research) mutual inductance bridge was used for the measurements. The magnitude of the ac magnetic field was estimated to about 2–4 Oe. In one series of experiments hydrostatic pressure (<2 GPa) was applied at room temperature by a standard piston-cylinder beryllium-copper clamp inserted into a liquid helium dewar for cooling. Fluorinert FC77 (3M) was used as a pressure-transmitting medium. The temperature was measured using either a k-type thermocouple inside the Teflon-pressure cell or, below 50 K, by a germanium thermometer mounted in the beryllium-copper clamp close to the sample position. The pressure was measured *in situ* at about 7 K by monitoring the T_c shift of a high-purity (99.9999 %) lead manometer. A second series of experiments was conducted measuring the same samples in a He-gas pressure cell ($p<1.2$ GPa, Unipress) inserted into a variable temperature cryostat (CRYO-Industries of America). Gas pressure was transmitted from a 1.5-GPa gas compressor (U11, Unipress) through a beryllium-copper capillary (ID 0.3 mm). Pressure can be changed at any temperature above the freezing temperature of the helium pressure medium. In particular, pressure was changed at low temperature where the interstitial oxygen is immobile. The temperature was controlled by preheated He gas in the cryostat, and measured by a thermocouple inside the pressure cell as well as by two thermometers attached to the top and bottom of the cell. Special care has been taken to avoid freezing of the helium in the capillary before it solidifies in the pressure cell. The pressure was measured using two manometers. A manganin gauge indicated the pressure at room temperature in the high-pressure chamber of the gas compressor. A second (semiconductor) manometer was mounted close to the sample inside the pressure cell. As long as the helium in the system is liquid, both manometers yield identical readings, as expected. However, if the helium solidifies in the pressure cell (this happens, e.g. at 38.7 K for $p=0.5$ GPa or at 61 K for $p=1.01$ GPa),[26] the *in situ* semiconductor gauge is extremely valuable to detect the pressure drop during freezing and any possible blockage of the capillary. We have found that even in the solid state of the pressure medium the internal gauge still yields reliable pressure readings following the known isochore of the helium solid.[26] Data were taken during cooling and heating through the superconducting transitions. The cooling speed between room temperature and 150 K was very slow (typically 0.4 K/min) in order to maintain exactly the same conditions for all experiments. This is particularly important for doping levels where chemical phase separations occur because it was shown that in this range the superconducting transition temperature may depend on the cooling rate.[27] However, any kinetic process leading to phase separations slows down at low temperature and prevents the sample from reaching true thermodynamic equilibrium at temperatures close to T_c. We have tested various cooling procedures with speeds below 0.4 K/min, and found no appreciable change in the superconducting properties. Therefore, we conclude that with the chosen procedure the samples are as close to thermodynamic equilibrium as one can get.

III. RESULTS AND DISCUSSION

A. Ambient pressure results

The dc susceptibility χ_{dc} was measured and compared with the real part of the ambient pressure ac susceptibility χ_{ac}. Although we did not attempt to extract the superconducting volume fraction from the ac measurements, we could show that the relative temperature dependence of χ_{ac} is comparable to that of χ_{dc}. The results obtained by the ac method for $La_2CuO_{4+\delta}$ reproduced our earlier dc data.[2] A single superconducting transition ($T_c \approx 30$ K) observed for low doping ($\delta<0.05$) turns into a two-step transition (T_c's at about 15 and 30 K) upon increasing δ. This effect was interpreted as a doping-induced electronic phase separation of two intrinsic superconducting states. At $\delta=0.082$ (corresponding to the hole concentration $n_h=0.125=1/8$) the superconducting volume fraction of the 30-K phase is greatly diminished but that of the 15-K phase is not changed.[28] This results in a fast drop of the onset—T_c for superconductivity from about 30 to 15 K at this special hole concentration in analogy to the so called 1/8 anomaly in the $La_{2-x}(Sr,Ba)_xCuO_4$ system. The phase diagram and some typical ac susceptibility curves are schematically shown in Fig. 1 as a function of n_h. Also shown in the bottom half of the figure are the same data for the Sr codoped system, $La_{1.985}Sr_{0.015}CuO_{4+\delta}$. The qualitative features of both systems are very similar. In particular, the transition from the one-T_c to the two-T_c regime in the diagram and the 1/8 anomaly occuss at the same hole concentration n_h but at different δ. Note that n_h here is the "nominal" "total" carrier density determined by the equation in Sec. I. Theses results reconfirm that our samples are indeed close to equilibrium, and that single- and double-T_c behaviors are "intrinsic" properties of doped holes. In the very low doping region ($n_h<0.06$) there is a major difference between the two sets of samples. There is a single $T_c=15$ K in $La_{1.985}Sr_{0.015}CuO_{4+\delta}$, whereas the T_c of $La_2CuO_{4+\delta}$ remains at 30 K even for the smallest δ. This change of T_c is explained by the attraction of charge carriers to the "frozen" Sr ions. Because of the random distribution of the cation dopants the formation of the $T_c=30$ K phase is inhibited. The Coulomb attraction between holes and Sr ions results in a more homogeneous distribution of carriers with a lower local hole density, and the intrinsic $T_c=15$ K phase is
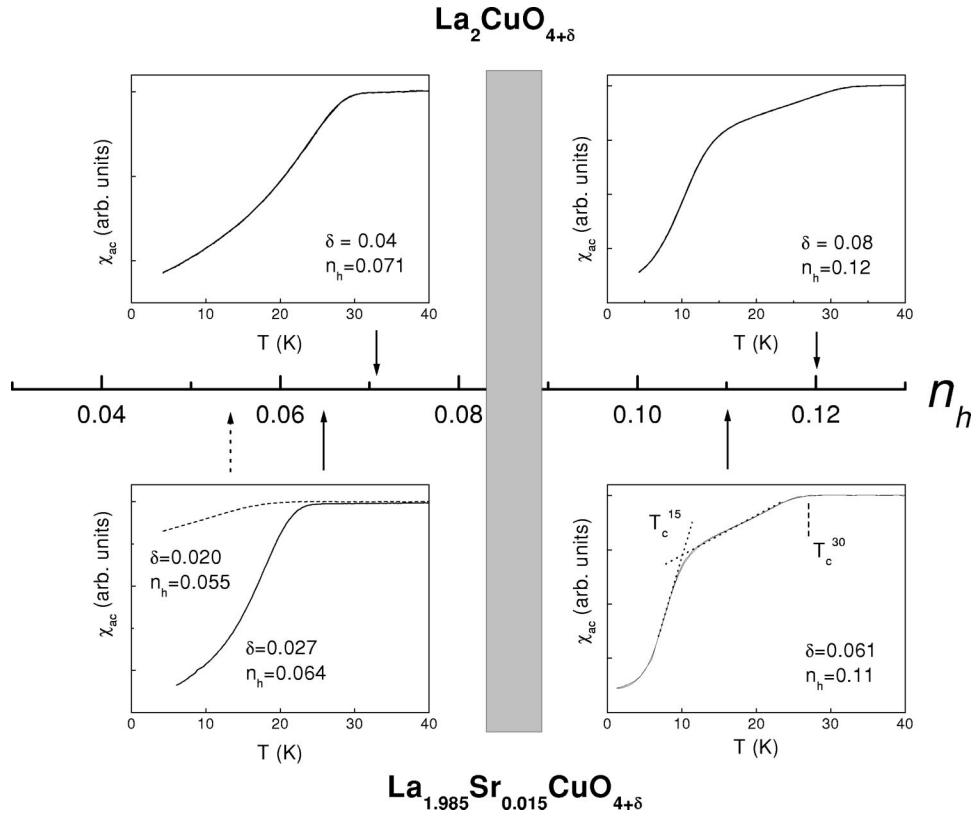
FIG. 1. Phase diagram of $La_{2-x}Sr_xCuO_{4+\delta}$. Typical examples of the real part of χ_{ac} are shown, and the arrows indicate the hole density in the diagram. The shaded area separates the two regions where one and two superconducting transitions are observed.

stabilized instead. In the following sections we discuss the pressure effects on the superconducting transitions in $La_{2-x}Sr_xCuO_{4+\delta}$ for various doping levels for the two characteristic regimes in the phase diagram (Fig. 1) and for samples with carrier density $n_h \approx 0.085$ located right at the transition boundary (the shaded area in Fig. 1).

B. Effect of high pressure on the superconducting transition: pressure applied at room temperature

The ac susceptibility data for two typical samples with $n_h \approx 0.068$ in the single $T_c = 30$ K regime are displayed for different pressures in Figs. 2(A) ($La_2CuO_{4.04}$) and 2(B) ($La_{1.985}Sr_{0.015}CuO_{4.027}$). The diamagnetic signal of χ_{ac} shifts to higher temperature, and allows for an accurate determination of the pressure coefficient of T_c, defined as the onset of the diamagnetic drop. The pressure effect on $\chi_{ac}(T)$ is reversible upon increasing and decreasing pressure, and reproducible in several pressure cycles. The pressure dependences of T_c for both samples (open circles) and also for $La_{1.985}Sr_{0.015}CuO_{4+\delta}$ at higher oxygen dopings, $\delta = 0.040$ (triangles) and $\delta = 0.061$ (squares), are shown in Fig. 3. The increase of $T_c(p)$ is nonlinear for small pressure but linear at larger pressure. The pressure coefficient (in the linear high-pressure range) is unusually large, 9–10 K/GPa. This is about 3–4 times larger than the dT_c/dp of the cation-doped $La_{2-x}(Sr,Ba)_xO_4$,[29] and appears to be the largest pressure coefficient observed in a La-214 high-T_c superconductor. An anomalous large dT_c/dp (up to 6 K/GPa) was previously

observed only near the 1/8 anomaly in the La-214 system, where the ambient pressure T_c is very low.[30] This huge pressure coefficient is obviously a consequence of the high mobility of the interstitial oxygen dopants. In the underdoped region, pressure is known to increase the transition temperature of high-T_c superconductors, even in systems without mobile oxygen such as $La_{2-x}(Sr,Ba)_xO_4$. For multilayer compounds this effect was frequently attributed to a pressure induced increase of the average hole density in the Cu-O planes due to a charge transfer from a charge reservoir block to the active layer. However, in the structure of La-214 there is no charge reservoir, and the average hole concentration does not change with pressure. One possibility to stabilize the superconductivity and to increase T_c is a phase separation into hole-rich and hole-poor phases. At ambient conditions, this phase separation in $La_2CuO_{4+\delta}$ results in phases with low and high oxygen contents and different lattice structures for low doping ($\delta < 0.05$), and in the coexistence of two superconducting phases ($T_c = 15$ and 30 K) for higher doping levels ($\delta > 0.05$).[2] Under pressure the higher $T_c = 30$ K state is favored and, with the support of the mobile oxygen ions, T_c may increase up to a rate of 10 K/GPa. In contrast, in the cation-doped system, $La_{2-x}(Sr,Ba)_xO_4$, the random distribution of the immobile dopants prevents the hole system from phase separation due to a pinning of holes close to the randomly distributed dopant sites. This explains the far lower pressure effect on T_c in that system. For the oxygen-doped as well as the oxygen-Sr codoped La-214 cu-
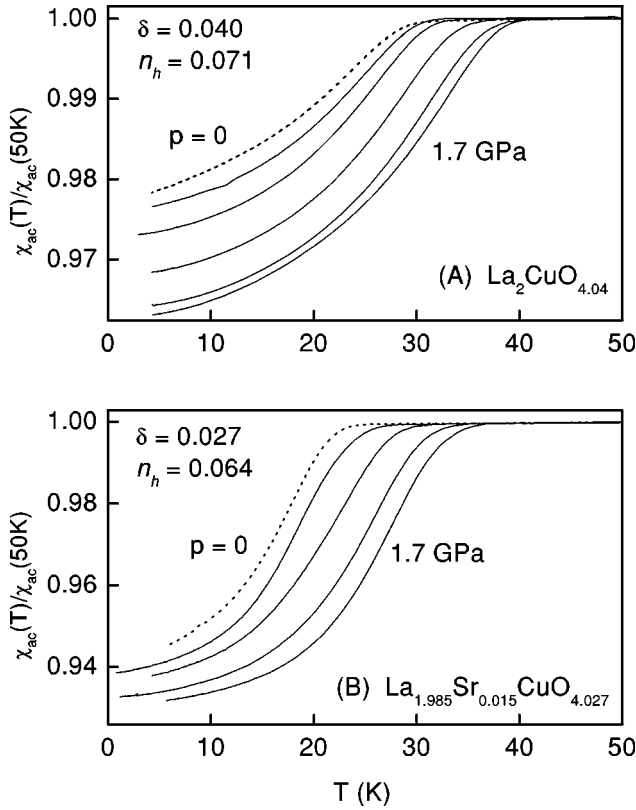
FIG. 2. Pressure effect on the real part of the ac susceptibility of La$_{2-x}$Sr$_x$CuO$_{4+\delta}$ in the one transition region (n_h<0.085). (A) La$_2$CuO$_{4.04}$. (B) La$_{1.985}$Sr$_{0.015}$CuO$_{4.027}$. The dotted curves show the ambient pressure data.

FIG. 4. Pressure effect on the real part of the ac susceptibility of La$_{2-x}$Sr$_x$CuO$_{4+\delta}$ in the two-transition region (n_h>0.085). (A) La$_2$CuO$_{4.08}$. (B) La$_{1.985}$Sr$_{0.015}$CuO$_{4.061}$. The dotted curves show the ambient pressure data.

prate, the pressure induces a redistribution of the strongly correlated interstitial oxygen and hole system. This results in a stabilization of the superconducting phase and the large dT_c/dp observed in our experiments. Similar effects have been reported in high-pressure experiments on underdoped
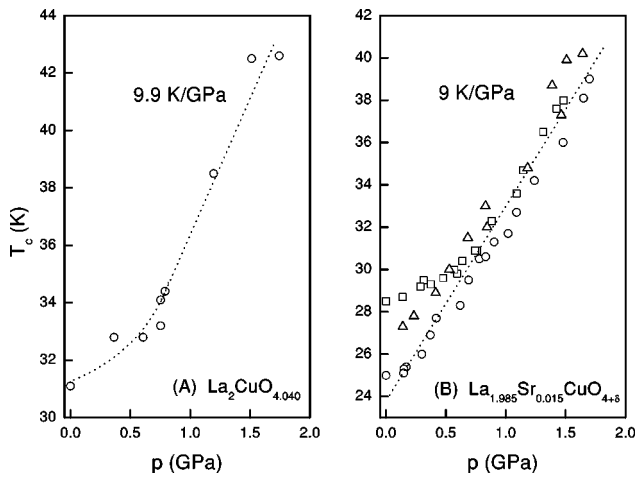

FIG. 3. Pressure dependence of T_c (defined as the onset of the diamagnetic drop) for the data of Fig. 2 (circles). Also shown in (B) are data for higher doping, δ=0.04 (triangles) and δ=0.061 (squares). The pressure coefficients given in the figure refer to the linear high-pressure part of $T_c(p)$.

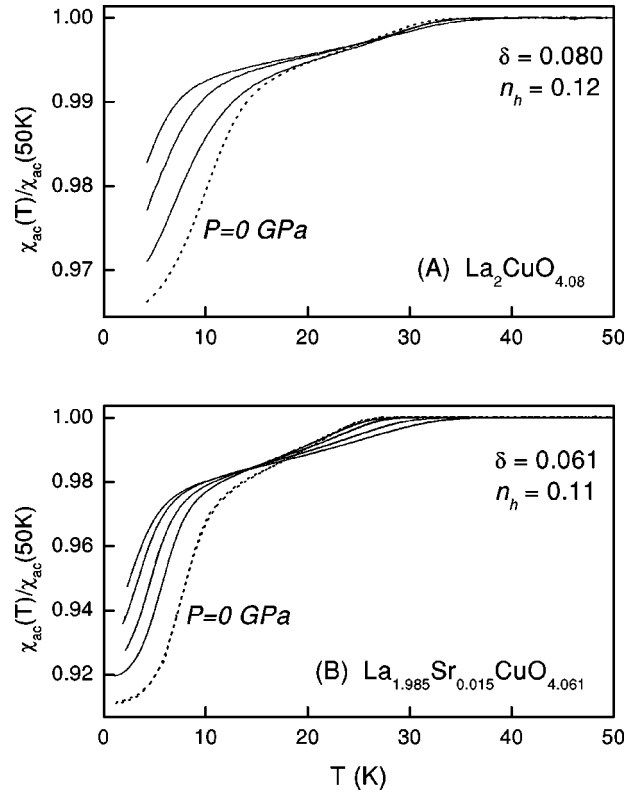YBa$_2$Cu$_3$O$_{7-\delta}$,[19] and may be due to the same underlying microscopic mechanisms.

In the high hole density (n_h>0.084) regime where we found two superconducting transitions with T_c=15 and 30 K coexisting at ambient pressure, the effect of pressure on the two transitions is of particular interest. Figure 4 shows the temperature dependence of the ac susceptibility at different pressures for two typical samples with n_h≈0.115, La$_2$CuO$_{4.108}$, and La$_{1.985}$Sr$_{0.015}$CuO$_{4.061}$. The typical two-step characteristics of $\chi_{ac}(T)$ is preserved under pressure, but the critical temperatures for both transitions are pushed into opposite direction, i.e., $T_c^{(30)}$ increases and $T_c^{(15)}$ decreases with pressure. Note that $T_c^{(30)}$ is defined as the onset of the diamagnetic drop of $\chi_{ac}(T)$, and $T_c^{(15)}$ is determined from the bending of the susceptibility curve as shown in the lower right graph of Fig. 1 (dotted lines). Thereby, under high pressure $T_c^{(30)}$ has the same pressure coefficient as that of δ<0.05 samples [see, e.g., Fig. 3(B)] suggesting that it is the same superconducting state. $dT_c^{(15)}/dp$ is negative and of the order of −4 K/GPa. We conclude that pressure enhances the electronic phase separation between the two superconducting phases because of a redistribution of charges and dopants in the coupled hole-oxygen system. The 30-K phase becomes more stabilized at the expense of the 15-K state. The pressure-induced changes to the hole distribution may result in a change of the superconducting volume fractions of both phases, but also in a change of the hole density

of each superconducting phase. The superconducting volume fraction cannot be extracted from ac susceptibility measurements, but it would be accessible by measuring the dc susceptibility (Meissner effect) under high pressure. However, a sole change of the volume fractions of both (15 and 30 K) phases should not affect the transition temperatures. Therefore, it appears more likely that pressure changes the local hole density of the two phases, for example, by increasing the hole concentration of the 30-K phase and reducing the hole density of the 15-K phase. This might explain the change of both T_c's; however, the current experiments cannot provide information about the local hole concentrations. We also cannot exclude the possibility that the 15-K phase might be overdoped resulting in a negative pressure coefficient of T_c, as known for many high-T_c compounds. However, the cation-doped La-214 system was shown to exhibit a positive dT_c/dp even for doping levels well above the optimum.[29,30] As we will see in Sec. III C, the rearrangement of charges is suppressed by freezing the interstitial oxygen ions in their ambient pressure positions.

The pressure effect in the transition region (shaded area in Fig. 1) located at $n_h \approx 0.085$ is of special interest. The ambient pressure susceptibility at this special hole density shows one single transition at $T_c \approx 30$ K (dashed lines in Fig. 5). However, Fig. 5 shows that under hydrostatic pressure this transition splits in two, indicating that the electronic phase separation can be induced by pressure. The relevant parameter for this effect is the hole density, n_h. Figures 5(A) and 5(B) compare two data sets for $La_2CuO_{4+\delta}$ and $La_{1.985}Sr_{0.015}CuO_{4+\delta}$ at almost the same $n_h \approx 0.083$, but different oxygen contents. The pressure-induced phase separation into 15- and 30-K superconducting phases is obvious in both the oxygen doped and the Sr-oxygen codoped samples. However, if both compounds are compared at the same δ but slightly different hole density [Figs. 5(A) and 5(C)], the pressure effect on the superconducting transition is qualitatively different. The splitting into two transitions is induced by pressure in $La_{1.985}Sr_{0.015}CuO_{4.04}$ but not in $La_2CuO_{4.04}$. This result indicates that the separation into two T_c's is hole driven. If those two T_c's were due to two distinct chemical phases, then we would expect to observe the two T_c's behaviors in samples with the same oxygen content, e.g., in $La_2CuO_{4.04}$. The small increase in the hole density due to the codoping with Sr triggers an interesting pressure effect at this special carrier density. This observation, coupled with the fact that all samples are close to thermal equilibrium and behave similarly at the same carrier density, leads us to the conclusion that the hole density dictates the superconducting properties of $La_{2-x}Sr_xCuO_{4+\delta}$, and indeed the two characteristic regimes are separated by a critical hole density $n_h \approx 0.085$. The observed phase separations at ambient and high pressures are driven by the system of holes, and are facilitated by the rearrangement of the mobile interstitial oxygen ions. It should be noted that all these effects cannot be observed in cation-doped $La_{2-x}(Sr,Ba)_xCuO_4$ because of the random distribution of the immobile dopant ions. Due to the Coulomb interaction between holes and dopant ions the hole
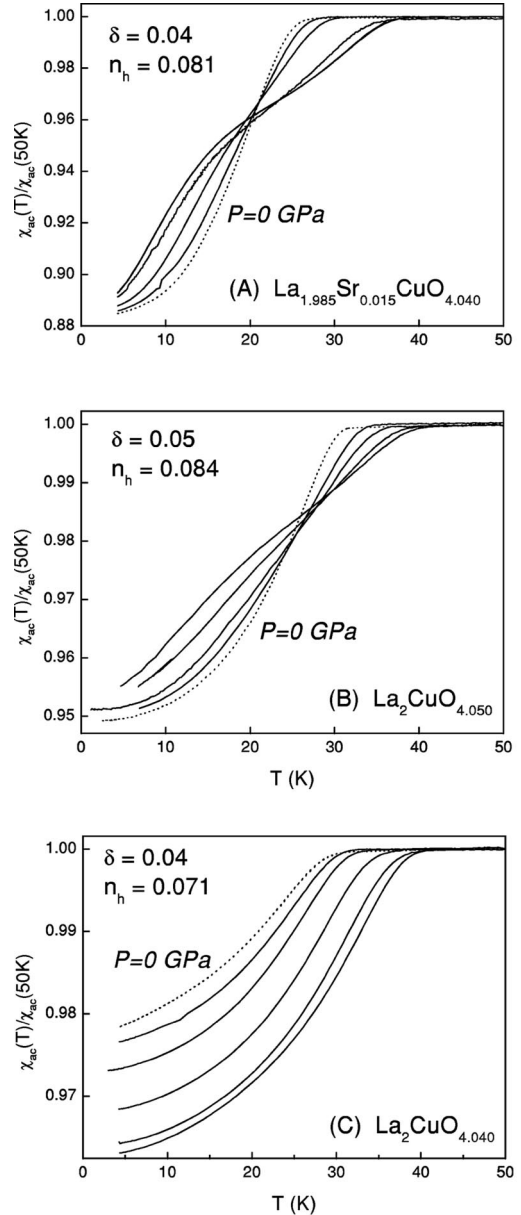

FIG. 5. Comparison of the pressure effect on the superconducting transitions in $La_{2-x}Sr_xCuO_{4+\delta}$ near the special hole density $n_h = 0.085$. (A) and (B) show that samples with different oxygen contents, δ but the same hole density behave very similarly under pressure. (A) and (C) compare samples with the same δ but slightly different n_h.

distribution in the Cu-O planes is affected by the dopants, and electronic phase separation into hole-rich and hole-poor phases is inhibited.

The pressure effects on the 15-K transition in $La_{1.985}Sr_{0.015}CuO_{4+\delta}$ (for $\delta < 0.024$ or $n_h < 0.06$) collaborates with our picture. From the former discussion it could be expected that pressure induces the phase separation into the hole-rich (30 K) and hole-poor (nonsuperconducting) phases. In fact, the ac susceptibility data of $La_{1.985}Sr_{0.015}CuO_{4.02}$ shown in Fig. 6 for pressures up to 1.74 GPa indicate that pressure rapidly increases the T_c

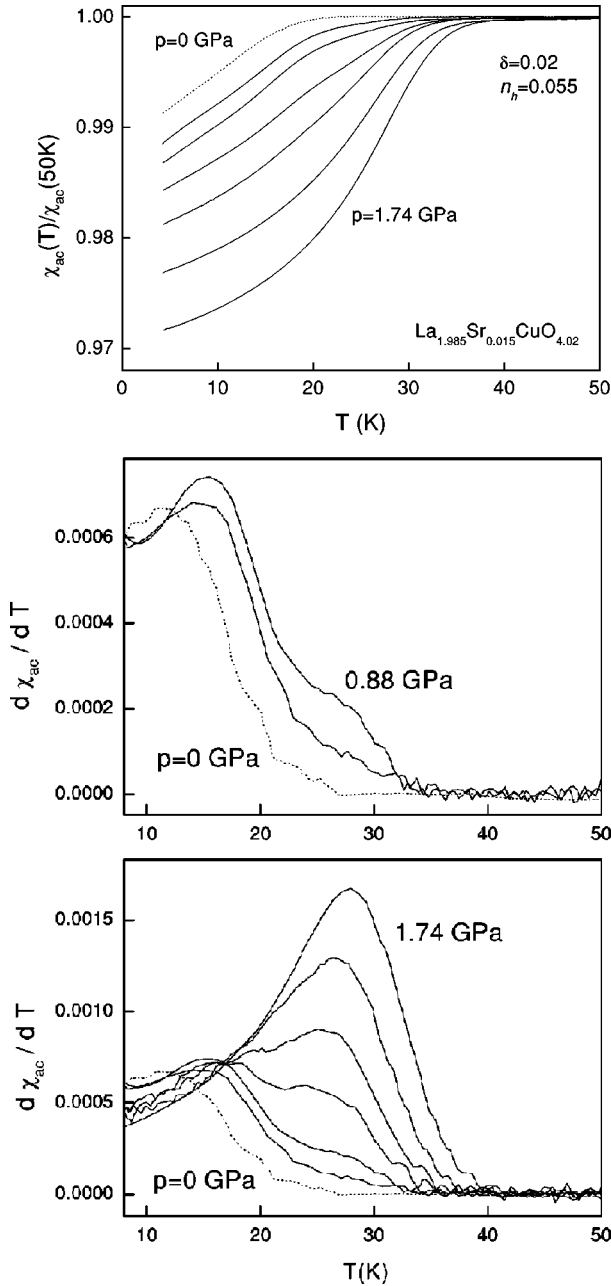FIG. 6. Pressure effect on the superconducting transition in $La_{1.985}Sr_{0.015}CuO_{4.02}$. (A) Real part of the ac susceptibility. The 30-K superconducting state grows under pressure at the expense of the ambient pressure 15-K state. (B) The derivative $d\chi_{ac}/dT$ revealing the details of the transition from the $T_c = 15$ K state to the $T_c = 30$ K state.

from 15 K to above 30 K. The details of this transition are clearly seen in the derivative, $d\chi_{ac}/dT$, displayed in Fig. 6(B). At ambient pressure (dashed curve in Fig. 6) $d\chi_{ac}/dT$ exhibits a single maximum close to 15 K as an indication of the diamagnetic drop of χ_{ac}. This maximum is shifted to higher temperature with increasing pressure [top part of Fig. 6(B)]. Above 0.6 GPa a shoulder appears in the temperature dependence of $d\chi_{ac}/dT$ at about 30 K. This shoulder corresponds to a small diamagnetic signal in χ_{ac} [Fig. 6(A)], and is interpreted as the pressure induced growth of the hole-

rich 30-K phase observed at the same hole density in $La_2CuO_{4+\delta}$. The sudden appearance of this $T_c = 30$ K state instead of a continuous increase of T_c from 15 to 30 K clearly demonstrates that there were two distinct intrinsic T_c's in this system. With a further increase of pressure this phase grows [the shoulder extends to a major peak in $d\chi_{ac}/dT$; see the bottom part of Fig. 6(B)], and becomes the major superconducting phase in the sample. There is a narrow pressure range ($p \approx 0.9$ GPa) where both phases coexist and the $d\chi_{ac}/dT$ curve exhibits two separated maxima. Since we have seen that the 30-K transition is favored under pressure, mobile oxygen dopants now facilitate a phase separation into hole-rich and hole-poor phases similar to the $La_2CuO_{4+\delta}$ system. This interesting pressure effect has been observed in $La_{1.985}Sr_{0.015}CuO_{4+\delta}$ for several samples with $\delta < 0.024$. To prove the conclusion of this section and to collect additional evidence for the role of interstitial oxygen, we investigate the pressure effects while oxygen ions are immobile.

C. High-pressure effect on the superconducting transition: pressure changed at low temperature

The mobility of the interstitial oxygen is greatly reduced and the ions are literally frozen in their positions if the temperature is reduced to below 100 K. Changing pressure at low temperature will allow us to separate the pressure effect on the electronic state from the effect of electronic phase separation facilitated by mobile oxygen ions. The low-temperature pressure change can be achieved by employing a helium gas-pressure cell connected to a gas compressor. For several typical $La_2CuO_{4+\delta}$ and $La_{1.985}Sr_{0.015}CuO_{4+\delta}$, samples the pressure effects (at $T < 100$ K) were investigated using three basic procedures:

(i) Pressure up to 1 GPa was applied at room temperature and released in several steps at low temperature. ac susceptibility measurements through the superconducting transition were conducted at each pressure step below 100 K.

(ii) Following the release of pressure below 100 K according to procedure (i), the samples were reheated to room temperature so that the mobile oxygen could rearrange. Samples were cooled again (without changing pressure) through the superconducting transition. The comparison of the two measurements shows the sole effect of interstitial oxygen redistribution on T_c.

(iii) Samples were cooled to low temperature at ambient pressure. Pressure was increased below 100 K, and the ac susceptibility was measured for each pressure.

The pressure shift of $T_c^{(30)}$ is shown in Fig. 7 for a typical sample in the low hole density region, $La_{1.985}Sr_{0.015}CuO_{4.027}$ ($n_h = 0.064$). The pressure in this experiment was raised to 1 GPa at room temperature and released at low T. During cooling the pressure drops to about 0.92 GPa at the freezing temperature of the helium pressure medium, $T_f = 55$ K. A further pressure decrease to 0.82 GPa at 35 K is due to the volume reduction and the isochoric change of state of the solid helium. $T_c(0.82$ GPa) coincides with the previous measurements [Fig. 2(B)], and decreases with decreasing pressure at a rate of 2.8 K/GPa. This rate is less than 1/3 of
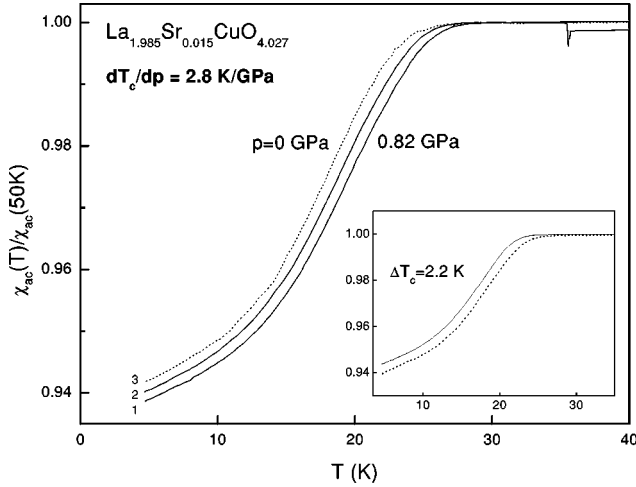
FIG. 7. Low-temperature pressure effect on the $T_c = 30$ K phase of $La_{1.985}Sr_{0.015}CuO_{4.027}$. 1 GPa pressure was applied at room temperature (curve 1) and released to zero (curve 3) below 100 K. The inset shows a further decrease of T_c by 2.2 K after the sample was reheated to room temperature (solid curve).

FIG. 8. Low-temperature pressure effect on the superconducting state in the two-T_c region, $La_{1.985}Sr_{0.015}CuO_{4.061}$. A 0.8-GPa pressure was applied at room temperature, and the pressure was varied between 0.93 GPa and zero below 100 K. The inset shows the change of the real part of $\chi_{ac}(T)$ after the sample was reheated to room temperature (solid curve).

that estimated in Sec. III B for the same sample [Fig. 3(B)]. After heating the sample to room temperature and cooling again, T_c is further reduced by 2.2 K (inset of Fig. 7). This additional change of T_c is a pure effect of oxygen redistribution since pressure was not changed. This shows that the hole-oxygen system was frozen in a metastable state after the release of pressure at low temperature, and could only relax toward thermal equilibrium after the temperature was raised high enough to allow the oxygen diffusion. Repeating the measurement according to procedure (iii) the increase of pressure from $p = 0$ at low temperature results in a similar shift of T_c at the rate of about 3 K/GPa, in good agreement with the value of 2.8 K/GPa mentioned above. We conducted the same series of gas-pressure experiments with the oxygen-doped $La_2CuO_{4.04}$ ($n_h = 0.071$), and found very similar results. Again, the observed pressure coefficient of $dT_c/dp \approx 2.7$ K/GPa was strongly reduced with respect to the value of 9.9 K/GPa found in Sec. III B for this sample [also see Fig. 3(A)]. It is interesting to note that the reduced dT_c/dp is comparable to the pressure coefficient of the cation-doped $La_{2-x}Ba_xCuO_4$ (2–3 K/GPa) and slightly larger than dT_c/dp for $La_{2-x}Sr_xCuO_4$ (≈ 1.5 K/GPa) for the doping region not too close to the 1/8 anomaly.[29,30] Therefore, we conclude that this pressure coefficient of $dT_c/dp \approx 2.7$ K/GPa should be considered as the pressure effect of the $T_c^{(30)}$ transition under the "hard doping," either Sr or frozen oxygen, condition.

For the higher doping region ($n_h > 0.085$) we choose a representative sample, $La_{1.985}Sr_{0.015}CuO_{4.061}$. Our clamp-cell data [Sec. III B, Fig. 4(B)] indicate that pressure enhances the phase separation. This effect cannot be observed if pressure is changed at low temperature. Figure 8 shows the temperature dependence of χ_{ac} at different pressures applied according to the following procedure: Pressure was increased at room temperature to 0.8 GPa. After cooling to low temperature pressure was varied below 100 K between 0.93 and 0.01 GPa. The two superconducting transitions are clearly
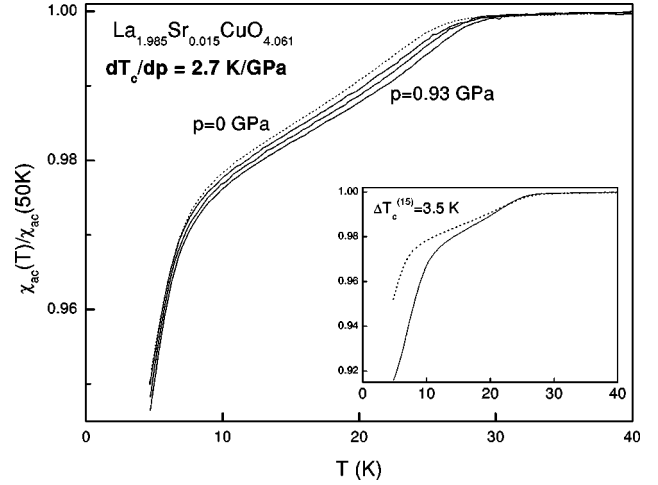
distinguished; however, pressure mainly affects $T_c^{(30)}$, whereas $T_c^{(15)}$ remains almost unchanged. The pressure coefficient $dT_c^{(30)}/dp = 2.7$ K/GPa is of the same value as that for the single transition compounds (for $n_h < 0.085$). After heating at 0.01 GPa to room temperature the superconducting properties of the sample changed and, in particular, $T_c^{(15)}$ increased by about 3.5 K, restoring the original ambient pressure curve $\chi_{ac}(T)$. Very similar data have been obtained for oxygen-doped samples with $n_h > 0.085$, e.g., $La_2CuO_{4.08}$. The freezing of the oxygen ions at low temperature prevents the pressure-induced enhancement of electronic phase separation as observed in the experiments described Sec. III B. Thermodynamically, the system behaves more like $La_{2-x}(Sr,Ba)_xCuO_4$ under pressure. The major difference is the inhomogeneous hole-oxygen distribution in $La_{2-x}Sr_xCuO_{4+\delta}$ we start with at ambient conditions. The degree of phase separation already present at ambient T is frozen and preserved at low temperature and cannot be changed by pressure.

For $n_h \approx 0.085$ (shaded area in Fig. 1) we have shown that pressure applied at room temperature facilitates oxygen diffusion, and induces the electronic phase separation. However, if oxygen is frozen at low T and pressure is changed below 100 K, we expect that the initial (room temperature) state is preserved. Figure 9 shows the pressure effect on $\chi_{ac}(T)$ for $La_2CuO_{4.055}$ ($n_h = 0.09$). In the first experiment low pressure (0.1 GPa) was applied at room temperature and the sample was cooled to low T [dotted curve 1 in Fig. 9(A)]. Then pressure was increased (below 100 K) to about 0.5 GPa [solid curve 2 in Fig. 9(A)]. The susceptibility curve shifts in parallel to higher temperature at a rate of 2.9 K/GPa. No broadening or splitting of the transition is observed. In the second experiment we applied 0.8 GPa at room temperature. The superconducting transition broadens [dotted curve, Fig. 9(B)] and indicates the tendency to split-
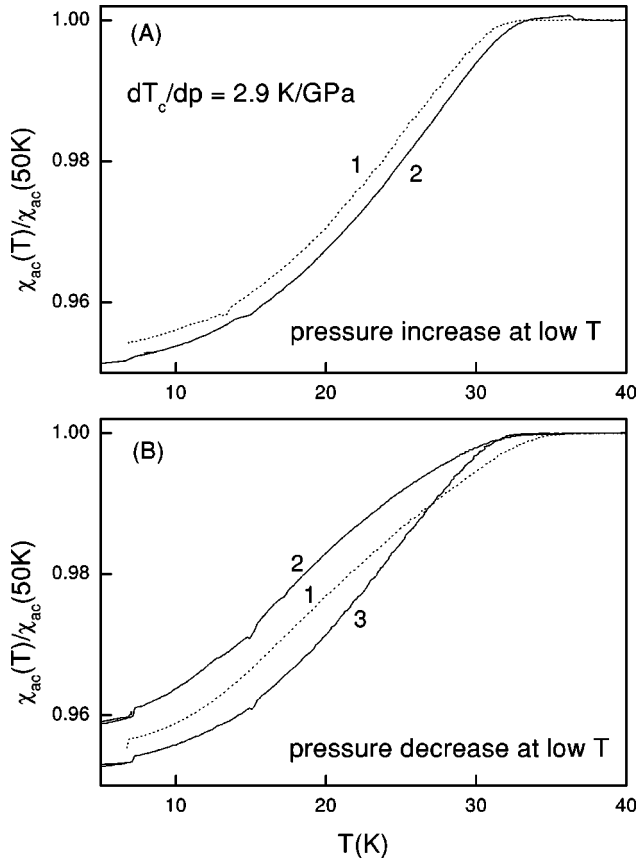
FIG. 9. Low-temperature pressure effects on the real part of the ac susceptibility of $La_2CuO_{4.055}$ ($n_h = 0.09$). (A) Pressure was increased from 0.1 GPa (curve 1) to 0.5 GPa (curve 2) at low temperature. (B) Pressure of 0.8 GPa was applied at room temperature (curve 1) and released to 0.1 GPa at low T (curve 2). The broadening and splitting into two transitions is preserved after a release of pressure. Reheating to room temperature initiates the oxygen diffusion, and the original 0.1-GPa state is recovered [curve 3, to be compared with curve 1 in (A)].

ting into two transitions due to the phase separation as seen in the previous section [Figs. 5(A) and 5(B)]. The release of pressure at low T to 0.1 GPa does not change the width or the shape of the diamagnetic susceptibility signal [curve 2, Fig. 9(B)]. The phase separation induced by pressure at high temperature is preserved. However, T_c shifts by about $2-3$ K. Heating the sample at 0.1 GPa to room temperature recovers the original (one-transition) state [curve 3, Fig. 9(B), which is comparable with curve 1, Fig. 9(A)] due to the rearrangement of the interstitial oxygen and hole system toward thermal equilibrium.

In Sec. III B we showed that in $La_{1.985}Sr_{0.015}CuO_{4.020}$ high pressure (applied at room temperature) induced the 30-K superconducting state at the expense of the 15-K phase. To show that this effect is also related to the rearrangement of the interstitial oxygen we measured the pressure effect using the He gas pressure apparatus. The experiment starts with applying high pressure of 1.1 GPa at ambient temperature. The ac susceptibility clearly shows the emerging 30-K phase at low temperature, as indicated by the shoulder in the derivative, $d\chi_{ac}/dT$, close to 30 K (curve 1, dotted line in Fig.
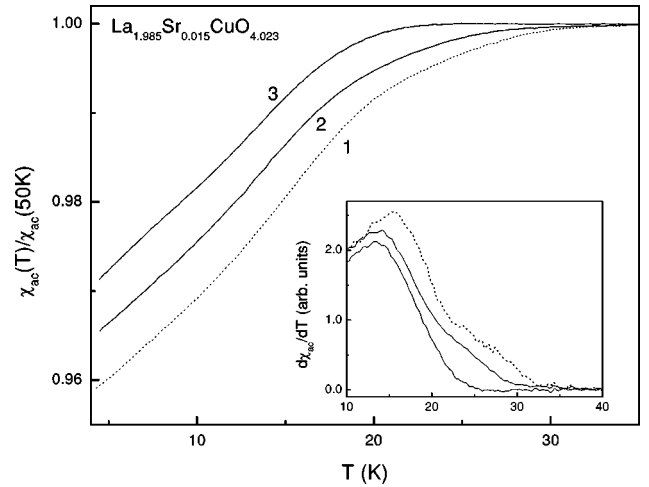

FIG. 10. Low-temperature pressure effects on the superconducting phases in $La_{1.985}Sr_{0.015}CuO_{4.023}$ ($n_h = 0.06$). A pressure of 1.1 GPa was applied at room temperature (curve 1), and completely released at low T (curve 2). The pressure induced a $T_c = 30$ K phase as indicated by the shoulder near 30 K in the derivative (inset), preserved at zero pressure. Reheating to room temperature allows the oxygen to redistribute and the 30 K phase again disappears (curve 3).

10). Although the pressure is not high enough to show the larger effect as in Fig. 6, the data are in good agreement with the clamp cell experiments at the same pressure. After releasing pressure completely (curve 2 in Fig. 10) the 30-K phase still survives at about the same amount. Only after heating the sample to room temperature (curve 3, Fig. 10) will the oxygen ions and the holes rearrange and the 30-K phase again disappears. This effect can only be explained by considering the pressure induced change of the interstitial oxygen distribution. High pressure stabilizes the hole-oxygen-rich phase with a higher (30 K) T_c. After cooling to below 100 K, and pressure release, the clustered oxygen ions cannot relax to their zero-pressure thermal equilibrium distribution. Pinning the holes to the O^{2-}-rich regions the amount of the 30-K phase is preserved. However, this state is not in global thermal equilibrium. Raising the temperature to ambient the diffusion of oxygen is initiated, and the hole-oxygen system relaxes closer to equilibrium. Now the hole system is affected by the randomly distributed and fixed Sr ions and the 15-K state dominates the superconducting properties.

IV. SUMMARY AND CONCLUSIONS

The pressure effect on the superconducting transitions of electrochemically doped $La_{2-x}Sr_xCuO_{4+\delta}$ was investigated for $x = 0$, and 0.015 with various δ's. We show a strong correlation between the hole carriers and the dopants. Cation and oxygen dopings are characteristically different. Hard doping using strontium creates a correlated dopant-hole state and inhibits the macroscopic phase separation. Soft doping using mobile interstitial oxygen, however, facilitates the tendency to phase separation into hole-rich and hole-poor phases. Accordingly, $La_{2-x}Sr_xCuO_{4+\delta}$ shows a rich phase diagram as function of doping. In particular, two character-

istic regimes can be distinguished. One superconducting transition ($T_c \approx 30$ K) is observed in the low doping regime, but two successive transitions at about 15 and 30 K appear in the higher doping regime. For the two different sets of samples with $x=0$ and 0.015 the two regimes are separated by a critical hole density, $n_h \approx 0.085$. Sr codoped $La_{1.985}Sr_{0.015}CuO_{4+\delta}$ shows a correlated superconducting phase at a low hole density ($n_h < 0.06$) with a lower $T_c \approx 15$ K due to the hole pinning effect of the Sr ions.

Pressure applied at room temperature increases the 30-K transition temperature $T_c^{(30)}$ at an unusually high rate of 9–10 K/GPa. In addition, the tendency toward electronic phase separation is strongly enhanced by pressure as indicated by the large positive $dT_c^{(30)}/dp$ and a negative pressure coefficient of the 15-K transition temperature $T_c^{(15)}$. It was shown that, for the special hole density $n_h \approx 0.085$, pressure induces the phase separation into two superconducting phases for both strontium contents: $x=0$ and 0.015. The data are interpreted as a cooperative effect of pressure on the electronic state, facilitating phase separation and the rearrangement of the interstitial oxygen which enhances the original pressure effect. We conclude that the electronic state of carefully annealed oxygen-intercalated La-214 is closer to thermal equilibrium due to the missing frustration of immobile dopant ions.

The latter conclusion is further supported by a series of experiments where pressure was varied at low temperature (below 100 K), inhibiting any oxygen diffusion. The pressure coefficients of T_c appeared to be much smaller (<3 K/GPa) and comparable to the cation-doped $La_{2-x}(Sr,Ba)_xCuO_4$ indicating that the lower dT_c/dp is an effect of charge pinning. It was also shown that pressure, if changed at low temperature, neither enhanced the tendency of phase separation observed for $n_h > 0.085$ nor induced phase separation at the special hole concentration of $n_h \approx 0.085$. We suppose that the immobile interstitial oxygen at low temperature act similarly as the (randomly distributed)

Sr cations, which may explain the reduced pressure effect on the electronic hole system.

It is interesting to note that the crossover from the single to double transition region in the phase diagram as well as the pressure effects discussed above appear at the same hole density for both systems, $La_2CuO_{4+\delta}$ and $La_{1.985}Sr_{0.015}CuO_{4+\delta}$, considered in this investigation. This implies that the "total" hole density is the relevant parameter determining the nature of the superconducting states as well as the pressure effects on it. For higher strontium contents, however, the effects of the Coulomb interaction with the Sr ions have to be taken into account. The results obtained at ambient and high pressures provide strong evidence of the importance of the interaction of holes and dopants in high-temperature superconductors. Soft dopants, like interstitial oxygen in La-214 or chain oxygen in YBCO, may facilitate a phase separation into hole-rich and hole-poor phases. Thermodynamically, soft dopants and holes should be considered as one global correlated system relaxing towards thermodynamic equilibrium at high enough temperatures. Hard dopants, however, cause a pinning of holes and prevent the electronic system from phase separating into phases with different hole densities.

As a final note, while electronic phase separation in a very low doping regime can be understood in terms of the picutre of Emery and co-workers,[15,16] the phase separations we observed at such high doping levels are especially peculiar because the system is electronically phase separated into two dictinct T_c's. This suggests that a distinct electronic structure exists for each different T_c, and begins to form at a temperature above 200 K.

ACKNOWLEDGMENTS

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