Phase Separation and Finite Size Scaling in $La_{2-x}Sr_xCuO_{4+\delta}$ $[0 \leq (x,\delta) \leq 0.03]$

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A study of the phase diagram and magnetic susceptibility $\chi(x,\delta,T)$ of the title system is reported. For $\delta \simeq 0.03$, *macroscopic* phase separation, below $\simeq 300$ K into superconducting $La_{2-x}Sr_xCuO_{4+\delta'}$ ($\delta' \simeq 0.08$) and nonsuperconducting $La_{2-x}Sr_xCuO_{4+\delta''}$ ($\delta'' \simeq 0.00$) phases, known to occur for $x=0$, disappears by $x \simeq 0.03$. The behaviors of the Néel temperature $T_N(x)$ and $\chi(x,T)$ of the antiferromagnetic phase ($0 \leq x \lesssim 0.02$, $\delta'' \simeq 0.00$) reveal a novel *microscopic* segregation of the doped holes in this phase into walls of hole-rich material separating undoped domains.

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The manner in which the antiferromagnetic (AF) insulator cuprate parent compounds evolve to become high-temperature superconductors upon doping continues to be a topic of extensive theoretical and experimental research [1]. Perhaps the simplest system for the study of this issue is $La_{2-x}Sr_xCuO_{4+\delta}$. The parent compound La_2CuO_4 ($x=\delta=0$) undergoes a second-order transition from the tetragonal K_2NiF_4 structure to an orthorhombically distorted one below $T_{O/T}=530$ K, and exhibits long-range canted AF order below a Néel temperature $T_N \simeq 300$ K [2]. Upon subjecting La_2CuO_4 to O_2 gas at a pressure of 0.1 to 3 kbar and temperature $T \simeq 575$–$800\,^\circ$C followed by furnace cooling, $La_2CuO_{4+\delta}$ is formed containing $\delta \simeq 0.03$ excess bulk oxygen [2–5]. This material exhibits *macroscopic* phase separation below $T_s \sim 260$–320 K into oxygen-rich $La_2CuO_{4+\delta'}$ ($\delta' \simeq 0.08$) which becomes superconducting below $T_c \simeq 35$ K, and insulating AF $La_2CuO_{4+\delta''}$ ($\delta'' \simeq 0.00$) with $T_N \simeq 250$ K $\sim T_s$ [2,4–6]. Thus, one signature of phase separation in a particular sample [2,5,6], which we utilize below, is the observation of both superconductivity below $\simeq 35$ K and AF ordering in the sample. Theoretical studies of doped holes in the CuO_2 planes of the cuprates have predicted phase separation to occur into no-hole and hole-rich phases, similar to that below T_s in $La_2CuO_{4+\delta}$ [7]; according to one such mechanism, the doped-hole segregation occurs because the decrease in overall exchange energy between the Cu^{+2} magnetic moments arising from the hole segregation outweighs the increase in kinetic energy of the inhomogeneous hole distribution [7].

On the other hand, in the absence of excess oxygen, macroscopic phase separation at low (Sr) doping levels has not been observed in $La_{2-x}Sr_xCuO_4$. T_N is depressed extremely rapidly from $\simeq 300$ K for $x=0$ to ~ 0 K by $x \simeq 0.02$; this doping also depresses $T_{O/T}$, but at a much lower rate such that $T_{O/T}=0$ by $x \simeq 0.2$ [2]. A regime of spin-glass-like magnetic ordering below $\simeq 10$ K is observed for $x \gtrsim 0.02$, and bulk superconductivity occurs for $0.1 \lesssim x \lesssim 0.25$, with maximum $T_c \simeq 38$ K for $x \simeq 0.15$–0.20 [2]. Little is known about the phase diagram of the $La_{2-x}Sr_xCuO_{4+\delta}$ system with $x,\delta > 0$.

Herein, we report a study with high resolution in x of the magnetic and structural phase diagram of $La_{2-x}Sr_xCuO_{4+\delta}$ in the low doping regime $0 \leq (x,\delta) \leq 0.03$, where doped holes are produced by Sr doping *and/or* doping with excess oxygen. We find that in samples with $\delta \simeq 0.03$, superconductivity disappears by $x \simeq 0.03$, and conclude that the (macroscopic) phase separation known to occur for $x=0$ no longer occurs above $x \simeq 0.03$. Further, for the AF phase $La_{2-x}Sr_xCuO_{4+\delta''}$ ($0 \leq x \leq 0.02$, $\delta'' \simeq 0.00$), we find that (i) T_N decreases as a power law in x, and (ii) the magnetic susceptibility $\chi(x,T)$ satisfies $\chi(x,T) = \chi\{f(x)[T-T_N(x)]\}$. Our analysis indicates that $T_N(x)$ and $\chi(x,T)$ *of the AF phase* are determined by finite size effects induced by doping, where a novel segregation of the doped holes in this phase occurs into walls of hole-rich material separating *microscopic* regions of undoped material.

Sixteen samples of nominal composition $La_{2-x}Sr_xCuO_{4+\delta}$ were prepared by conventional solid state reaction at $1050\,^\circ$C using predried La_2O_3, $SrCO_3$, and CuO, in x increments of 0.002 from $x=0$ to 0.030. For each x value, the sample was separated into three parts which were treated at $650\,^\circ$C for 5 h in 1 bar N_2 or in 1 bar O_2, or at $500\,^\circ$C for 72 h in 230 bar O_2, respectively, and then oven cooled. $T_{O/T}$ was measured using a Perkin-Elmer differential scanning calorimeter [8]. Oxygen contents were measured by hydrogen reduction using a Perkin-Elmer thermogravimetric analyzer; the 1 bar N_2, 1 bar O_2, and 230 bar O_2 annealed series showed $\delta = 0.00(1)$, 0.01(1), and 0.03(1), respectively. Magnetizations were measured using a Quantum Design SQUID magnetometer.

We first present our results relating to the conventional phase diagram of $La_{2-x}Sr_xCuO_{4+\delta}$. Figure 1(a) shows $\chi(T)$ data ($H=5$ kG) for the samples annealed in 1 bar O_2. The downturns in the data below $\simeq 40$ K result from the onset of the superconductivity (see below). The $\chi(T)$ data for the other two series of samples (not shown) are similar, except that the series annealed under 1 bar N_2 showed no trace of superconductivity for any of the samples. T_N is the temperature of the peak in $\chi(T)$ [9]. The T_N values are plotted versus x in Fig. 2(a) for the three series of samples. For each series, T_N decreases to ~ 0 K

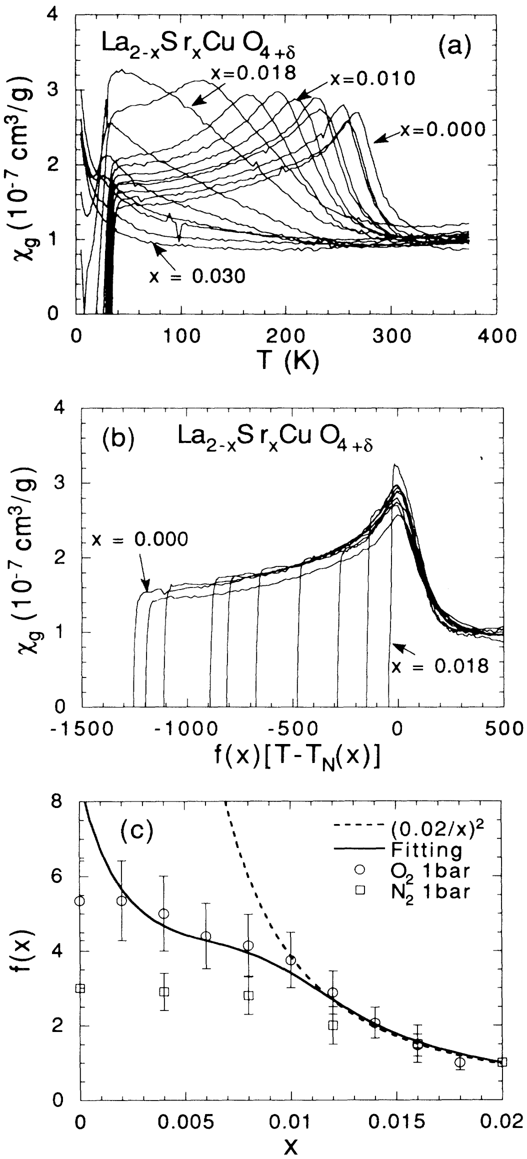

FIG. 1. (a) Magnetic susceptibility χ_g vs temperature T for $La_{2-x}Sr_xCuO_{4+\delta}$ samples annealed in 1 bar O_2. (b) χ_g data from (a) plotted with a scaled T axis. (c) The scaling function $f(x)$ in (b) vs x for the two series of samples annealed in 1 bar O_2 or 1 bar N_2; the dashed line is a $1/x^2$ dependence and the solid curve is a fit of Eq. (8) to the data for the former series.

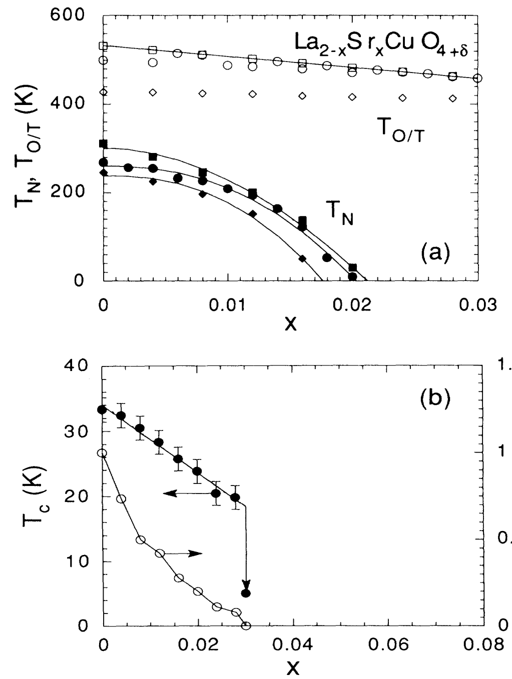

FIG. 2. (a) Phase diagram for $La_{2-x}Sr_xCuO_{4+\delta}$ samples annealed in 1 bar N_2 (squares), 1 bar O_2 (circles), and 230 bars O_2 (diamonds). The T_N data above 50 K are the $\chi(T)$ peak temperatures in Fig. 1(a), and those below 50 K were found either from ^{139}La nuclear quadrupole resonance measurements [Ref. [16] and F. C. Chou *et al.* (unpublished)] or estimated from Figs. 1(a) and 1(b). The straight line is a linear fit by $T_{O/T}(x)$ for the series annealed in 1 bar N_2, $T_{O/T}(x) = 532.4(3)\ \mathrm{K} - [2468(16)\ \mathrm{K}]x$, and the three curves are power-law fits [Eq. (1)] by $T_N(x)$. (b) Superconducting onset temperature (T_c) and Meissner fraction at 5 K ($-4\pi\chi$) vs x for the series annealed in 230 bars O_2. The solid circle with the arrow above it at $x=0.030$ denotes that no superconductivity was observed above 5 K for this sample.

by $x \simeq 0.02$. Also plotted in Fig. 2(a) is $T_{O/T}(x)$ for the three series. $T_{O/T}$ is seen to be very sensitive to δ, as observed previously for $La_2CuO_{4+\delta}$ [2]; the data for the 1 bar N_2 annealed series are in agreement with previous reports [8].

As noted above, the 1 bar N_2 annealed series $La_{2-x}Sr_xCuO_{4+\delta}$ ($\delta \simeq 0$) shows no evidence of superconductivity about 5 K, confirming that macroscopic phase separation does not occur for $\delta=0$ [2,5,6]. This result is in contrast to the behavior of the 1 and 230 bar O_2 annealed series ($\delta \simeq 0.01$ and 0.03, respectively), which do exhibit superconductivity. The maximum Meissner fractions in $H=50$ G were observed at $x=0$ and were about 0.1 and 1 vol.% for the latter two series, respectively. Here, the apparent superconducting fractions from Meissner effect data are known to underestimate the actual superconducting fractions, due to the comparable sizes of the London penetration depth and the phase separated superconducting regions [5]. $T_c(x)$ and the Meissner fraction versus x for the 230 bar O_2 annealed series ($\delta \simeq 0.03$) are shown in Fig. 2(b). T_c decreases linearly with x, but is nonzero ($\simeq 20$ K) as the Meissner fraction approaches zero at $x \simeq 0.03$. For $\delta \simeq 0.03$, we therefore conclude that the known phase separation for $x=0$, which produces the oxygen-rich superconducting phase, no longer occurs above $x \simeq 0.03$, and possibly above 0.02. That long-range AF ordering does not occur above $x \simeq 0.020$, whereas superconductivity is observed up to $x \simeq 0.028$, indicates that if phase separation does occur over the larger range $x \lesssim 0.028$, then the low-temperature state is a mixture of the spin-glass-like and superconducting phases for $0.020 \le x \le 0.028$, rather than the mixture of AF and superconducting phases occurring for $x \lesssim 0.020$.

We turn now to quantitative analysis and interpretation of $T_N(x)$ and $\chi(T)$ in Figs. 2(a) and 1(a), respectively, for the AF phase $La_{2-x}Sr_xCuO_{4+\delta''}$ ($0 \le x \lesssim 0.02$, $\delta'' \simeq 0.00$). For each series, the $T_N(x)$ data can be fitted with $n \simeq 2$ in the expression

$$1 - T_N(x)/T_N(0) = (x/x_c)^n , \tag{1}$$

where $T_N(0) = 301(9)$ K, $x_c = 0.0212(3)$, and $n = 1.90(20)$ for the 1 bar N_2 annealed samples, $T_N(0) = 261(7)$ K, $x_c = 0.0203(1)$, and $n = 2.33(19)$ for the 1 bar O_2 annealed samples, and $T_N(0) = 239(8)$ K, $x_c = 0.0177(3)$, and $n = 2.40(36)$ for the 230 bar O_2 annealed samples; the least-squares fits are shown as the solid curves in Fig. 2(a) [10].

Insight into the mechanism of the observed decrease in T_N with x in Fig. 2(a) can be gained by noticing that the power-law dependence in Eq. (1) is expected from finite size scaling theory [11], which predicts that the measured T_N is limited by the finite size (linear dimension L) of a system. In particular, this theory predicts [11]

$$1 - T_N(L)/T_N(\infty) \propto L^{-1/\nu} , \tag{2}$$

where, in mean-field theory, the exponent $\nu = \frac{1}{2}$. Equations (1) and (2) are consistent with $L(x) \propto 1/x^{n\nu}$. We interpret this consistency to mean that the doped holes form walls separating domains of undoped material (see also below), where the magnetic coupling between domains is much weaker than within a domain. Mean-field theory should hold in our case, because the long-range AF order below T_N results from weak coupling between strongly short-range-AF-ordered CuO_2 planes [2]. Since $n \simeq 2$ from above and $\nu = \frac{1}{2}$, one obtains $L(x) \propto 1/x$. This dependence $L(x) \propto 1/x$ indicates that the width of a wall is independent of x.

We turn now to the $\chi(T)$ data in Fig. 1(a). The peak associated with the canted AF ordering [2] in $La_{2-x}Sr_xCuO_{4+\delta''}$ becomes broadened, as well as depressed in temperature, with increasing Sr doping x. At the same time, the height of the peak is almost independent of x. This suggests [12] that the $\chi(T)$ data for all compositions $0 \le x \lesssim 0.02$ of the AF phase follow a scaling relationship

$$\chi(x,T) = \chi\{f(x)[T - T_N(x)]\} . \tag{3}$$

This scaling is indeed obeyed well both above and below T_N as shown in Fig. 1(b), where the data in Fig. 1(a) for all samples collapse onto a single curve obeying Eq. (3) (except for the data associated with the sueprconducting phase at the lowest T). The $\chi(T)$ data for the 1 bar N_2 annealed series of samples can be scaled equally well in the same way (not shown), but the data for the 230 bar O_2 annealed series cannot; the latter behavior is attributed to interference from the χ anomaly arising from the phase separation at T_s into AF and superconducting phases [6]. The scaling functions $f(x)$ for the first two series are shown in Fig. 1(c).

To explore the significance of the scaling in Eq. (3) and Fig. 1(b), we first note that $\chi(T)$ for La_2CuO_4 above T_N can be fitted with the mean-field expression $\chi(T) = \chi_0 + 4\chi_0^2(J^{bc})^2\chi_{\ddagger}^{+}(T)$ [9], where χ_0 is the nearly T-independent uniform susceptibility of the uncanted system and J^{bc} is an exchange anisotropy between adjacent Cu atoms. From the highest T data in Fig. 1(a), χ_0 is seen to be nearly independent of Sr doping (x) over our doping range. The staggered susceptibility $\chi_{\ddagger}^{+}(T)$ is given by [9]

$$[\chi_{\ddagger}^{+}(T)]^{-1} = J' + k_B T/(\xi/a)^2 , \tag{4}$$

where J' is the interplanar exchange constant. $\xi(T)$ is the AF correlation length within the CuO_2 planes, and a is the intraplanar nearest-neighbor Cu-Cu distance. The value of $\xi(T)$ in the absence of doping $[\xi_0(T)]$ is [13]

$$\xi_0/a = C_\xi \exp(2\pi\rho_s/k_B T) , \tag{5}$$

where $C_\xi = 0.276$, ρ_s is the spin stiffness constant, $2\pi\rho_s \simeq J$, and $J \simeq k_B(1500\text{ K})$ [2] is the intraplanar Cu-Cu exchange constant. According to our interpretation below Eq. (2), $\xi(T)$ is limited to a maximum value of order the domain size L. We first consider the mesoscopic (x,T) regime $a \ll L \ll \xi_0(T)$ (i.e., $x \gtrsim 0.01$, $T \lesssim 200$ K), for which $\xi = L$, and Eq. (4) becomes

$$[\chi_{\ddagger}^{+}(T)]^{-1} = 2J' + k_B[T - T_N(x)]/[L(x)/a]^2 , \tag{6}$$

where we have used the mean-field result $k_B T_N \sim J'(L/a)^2$ [9]. Thus, $\chi_{\ddagger}^{+}$ and χ become universal functions of $f(x)[T - T_N(x)]$, independent of x, if $f(x)$ is identified with $L^2(x)$. Above $x \simeq 0.01$, $f(x) \propto 1/x^2$ as shown by the dashed line in Fig. 1(c), which gives $L(x) \propto 1/x$, consistent with the form of $L(x)$ found above from our analysis of $T_N(x)$. The scaling property in Fig. 1 and Eq. (3) and our $T_N(x)$ data in Fig. 2(a) are inconsistent with a discontinuous change of $T_N(x)$ from 150 to ~ 10 K near $x = 0.017$ as proposed in Ref. [14].

The saturation of $f(x)$ in Fig. 1(c) below $x \simeq 0.01$ can be *qualitatively* understood within the above framework as arising from the T dependence of ξ, where significant T dependence below 400 K is expected to occur for $T_N \gtrsim 200$ K ($x \lesssim 0.01$) [15]. For $x = 0.02$–0.04, analysis of inelastic neutron scattering data showed that $\kappa(x,T) = 1/\xi(x,T)$ could be well described by the empirical relation [15]

$$\kappa(x,T) = \kappa(x,0) + \kappa(0,T) , \tag{7}$$

where $\kappa(0,T) = 1/\xi_0(T)$ and we identify $\kappa(x,0)$ with $1/L(x)$. From Eq. (7), one finds that the scaling property in Eq. (3) is satisfied if

$$f(x) \propto \{x + C/\xi_0[T_N(x)]\}^{-2}, \tag{8}$$

where we have approximated $\xi_0(T)$ by $\xi_0[T_N(x)]$, and $L(x)$ by C/x from Fig. 1(c) and our analysis of $T_N(x)$ above. For small T_N (large x), Eq. (8) yields $f(x) \propto 1/x^2$ as above, whereas for large T_N (small x), $f(x)$ tends towards a constant value. The solid curve in Fig. 1(c) is a plot of Eq. (8) for the 1 bar O_2 annealed series, using Eq. (5) and $J/k_B = 1600$ K.

Finally, we note that the $\xi(x,T)$ data for $La_{2-x}Sr_xCuO_4$ ($0.02 \le x \le 0.04$) inferred from the inelastic neutron scattering measurements [15], described empirically by Eq. (7), are themselves consistent with our model. The spin correlations within an (undoped) domain [i.e., with $r \lesssim L(x)$] satisfy $\langle \mathbf{S}(r)\cdot\mathbf{S}(0)\rangle \sim \exp[-r/\xi_0(T)]$, whereas $\langle \mathbf{S}(r)\cdot\mathbf{S}(0)\rangle \sim 0$ if $r \gtrsim L(x)$. In this case, we find that $\xi(x,T) \sim \xi_0(T)\{1-\exp[-L(x)/\xi_0(T)]\}$. This expression is found to describe the $\xi(x,T)$ data [15] equally well as Eq. (7). Domain formation for $0.02 \le x \le 0.08$ was also recently inferred based on ^{139}La NQR data [16,17].

From the present work, we conclude that the doped holes *in the AF phase* $La_{2-x}Sr_xCuO_{4+\delta''}$ ($0 \le x \lesssim 0.02$, $\delta'' \simeq 0.00$) condense into walls separating *microscopic* undoped domains, producing an electronically and magnetically inhomogeneous state, as predicted theoretically [7]. This novel doping-induced finite size effect provides a natural physical basis for understanding the anomalously strong depression of T_N and the strong reduction of the zero-temperature ordered magnetic moment in the AF phase with hole doping [2]. It will also be important to see whether similar effects are present in the superconducting compositions $x \sim 0.15$ of this system.

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