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Phase Separation and Doped-Hole Segregation in $La_2CuO_{4+\delta}$ and $La_{2-x}Sr_xCuO_{4+\delta}$*

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Herein, we review the magnetic, superconducting and structural phase diagrams of the title systems, with an emphasis on our recent results from magnetic and structural neutron diffraction, magnetic susceptibility and ^{139}La nuclear quadrupole resonance measurements. The results clarify the miscibility gap in the $La_2CuO_{4+\delta}$ system, and indicate the occurrence of frustrated phase separation on a nanoscopic length scale in the $La_{2-x}Sr_xCuO_4$ system with $0 < x \lesssim 0.05$.

1. INTRODUCTION

Above T_O = 530 K, the non-metallic compound La_2CuO_4 has the tetragonal K_2NiF_4 structure. Below this temperature, a second-order orthorhombic structural distortion occurs resulting from tilting of the CuO_6 octahedra. The stoichiometric compound exhibits long-range antiferromagnetic (AF) order below the Néel temperature $T_N \approx$ 325 K, and strong short-range dynamic two-dimensional (2D) AF order within the CuO_2 planes above T_N. Subjecting polycrystalline or single crystal La_2CuO_4 to high oxygen pressure at > 500 °C results in oxygen doped samples $La_2CuO_{4+\delta}$. The excess oxygen atoms occupy interstitial sites between adjacent LaO layers, and are located at the centers of La tetrahedra. Upon cooling below a temperature $T_{ps} \sim$ 300 K, compositions of $La_2CuO_{4+\delta}$ with $\delta \sim 0.03$ phase-separate into an antiferromagnetic insulator phase with $\delta' \approx 0.01$ and with $T_N \sim$ 250 K, and a metallic phase with δ'' estimated to be in the range 0.05-0.08 and with superconducting transition temperature $T_c \sim$ 35 K. For reviews of the above work, see e.g. Refs. 1 and 2.

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It is important to identify the microscopic interactions driving the phase separation in $La_2CuO_{4+\delta}$, since these interactions may also be present in the metallic cuprate compositions exhibiting high temperature superconductivity and may therefore contribute to the superconducting mechanism. In this paper, we review our recent work which addresses this issue.

2. THE T-δ PHASE DIAGRAM OF $La_2CuO_{4+\delta}$

The structural phase diagram of $La_2CuO_{4+\delta}$, determined from neutron diffraction measurements on polycrystalline electrochemically oxidized [3] samples, is shown in Fig. 1 [4]. At $T \sim 150$-200 K, the miscibility gap limits were found to be $\delta \approx 0.01$ and $\delta \approx 0.06$ as shown in the figure. The vertical sides of the miscibility gap at lower temperatures is probably due to loss of mobility of the excess oxygen. A significant feature of the data is a cusp near the center of the miscibility gap; the maximum T_{ps} found was 415 K for $\delta = 0.03_2$; this value of T_{ps} is significantly higher than the previous maximum reported value $T_{ps} \approx 320$ K [5]. The miscibility gap boundaries in Fig. 1 are identical within the errors with those found by Hammel et al. from NMR measurements on a phase-separated single crystal produced under high oxygen pressure [6]. Superconducting and normal state χ(T) measurements have shown that within the miscibility gap, the $T_N \approx 250$ K of the oxygen-deficient phase and the $T_c \approx 34$ K of the oxygen rich phase are nearly independent of overall composition δ, as expected [2].

A combined structural and magnetic neutron diffraction study was carried out on a single crystal produced by annealing under 3 kbar oxygen at 575 °C [7]. The crystal showed $T_O \approx 350$ K, $T_{ps} = 260 \pm 5$ K and $T_N = 245 \pm 3$ K. These results show that long-range AF ordering cannot be the driving force for the phase-separation transition, since in this case one would expect $T_N > T_{ps}$.

We have also studied the structure and properties of single crystal [8] and polycrystalline [2,9] samples at higher δ values than

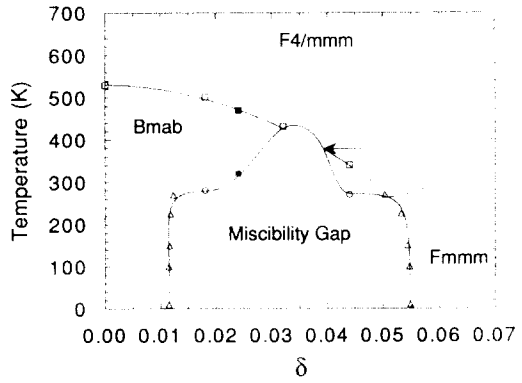

Figure 1. Phase diagram of $La_2CuO_{4+\delta}$ [4].

studied in Fig. 1. The T_c increases from ≈ 34 K for $\delta \approx 0.06$-0.08 to 40-45 K for $\delta \approx 0.11$-0.12, and both T_c's are observed for intermediate compositions. These data indicate that a two-phase region exists between these ranges of δ values. Neutron diffraction measurements on powders with $\delta \approx 0.08$ ($T_c = 32$ K) and $\delta \approx 0.12$ ($T_c = 42$ K) showed that these samples remained single-phase to 10 K, consistent with their compositions being beyond the upper miscibility gap boundary in Fig. 1 [10]. In addition, superstructure reflections were observed for these samples and for a crystal with $\delta \sim 0.1$, suggestive of oxygen ordering effects. Measurements of T_c under pressure indicated a thermal- and pressure-history dependent charge transfer from the LaO layers to the CuO_2 layers [11]. Measurements of the temperature-history and time-dependence of χ suggest that significant excess oxygen atom mobility develops, and therefore phase separation can proceed, above ~ 150 K [12].

To investigate how the phase separation transition is influenced by substitution of Sr for La, a study of the system $La_{2-x}Sr_xCuO_{4+\delta}$ was carried out with δ fixed at $\delta \approx 0.03$ [13]. The superconducting fraction was found to decrease to zero at $x \approx 0.03$, at which point T_c had decreased to about 20 K. These data indicate that for relatively small additional hole-doping (0.03 holes/Cu), T_{ps} is suppressed to below ~ 150-200 K where the excess oxygen mobility is lost.

3. MAGNETIC PHASE DIAGRAM OF LIGHTLY DOPED $La_{2-x}Sr_xCuO_4$ ($0 \le x \le 0.05$)

3.1. The antiferromagnetic regime $0 \le x \le 0.02$

As is well-known, the long-range AF order at $T_N \approx 325$ K in La_2CuO_4 is depressed to ≈ 0 K in $La_{2-x}Sr_xCuO_4$ by $x \approx 0.02$, although short-range dynamic AF order survives [1,2]. Using χ(T) and ^{139}La NQR measurements, we have determined $T_N(x)$ to high precision and found that $T_N(x) \approx T_N(0)$ [1 - $(x/x_c)^2$], where $x_c \approx 0.02$, as shown in Fig. 2 [13,14]. Further, $\chi(x,T)$ was found to scale as $\chi(x,T) = f(x)g[T - T_N(x)]$, where $f(x)$ is an empirically determined function of composition x and $g(T)$ is a universal function of temperature T, independent of x [13]. Independent analyses [13,14] indicated that the composition dependences of both $T_N(x)$ and $f(x)$ arise from a nanoscopic segregation of the doped holes into walls separating weakly-coupled dynamically AF ordered undoped domains within the CuO_2 planes, where the linear size L of the domains varies as $L(x) \alpha 1/x$. Thus, these data indicate that the doped holes are not randomly distributed; rather, the domains and domain walls form a configuration which is electronically and magnetically inhomogeneous on a nanoscopic scale.

From electrical resistivity measurements below T_N, the doped holes are found to localize upon cooling below ~ 50 K [15]. This implies that the above domain walls may be destroyed below this T. At still lower T, the ^{139}La NQR for $La_{2-x}Sr_xCuO_4$ with $x < 0.02$ shows a strong peak in the spin-lattice relaxation rate R_1 at a temperature $T_f < 16$ K which is proportional to x: $T_f(x) = (815\ \text{K})x$, as shown in Fig. 2 [14]. This peak was identified as arising from freezing of the spin degrees of freedom associated with the localized doped holes. This identification was recently confirmed theoretically by Gooding et al., who reproduced our observed $T_f(x)$ to high precision [16]. In their model, the effective spin degrees of freedom associated with the doped holes are the transverse (to the AF easy axis) components of the Cu spins in the vicinity of the holes. We conclude that below T_f, the spin-glass ordering of the effective doped-hole spins coexists with the long-range AF ordering of the (longitudinal components of the) Cu spins. The spin degrees of freedom of the doped holes and of the AF ordered Cu spins are thus distinct from each other, in contrast to the metallic doping regime ($x \gtrsim 0.1$) where it is widely believed that the Cu and doped-hole spins combine to form a single unique spin degree of freedom of the system.

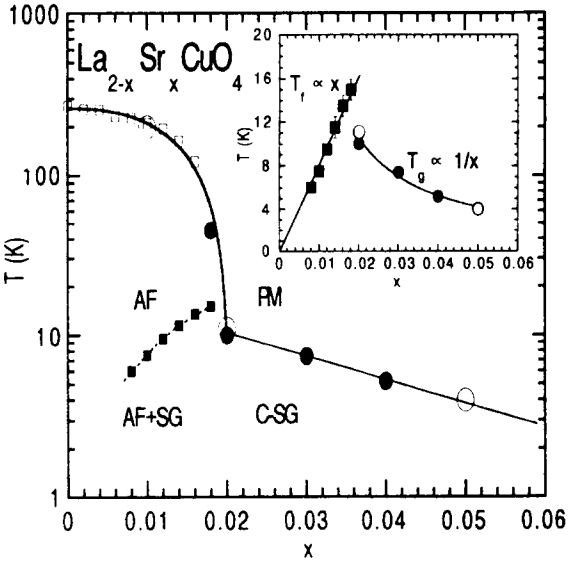

Figure 2. Magnetic phase diagram of lightly-doped $La_{2-x}Sr_xCuO_4$ [13,14]. Abbreviations: PM (paramagnetic), AF (antiferromagnetic), SG (spin glass), CSG (cluster spin glass), T_f (spin glass freezing temperature), T_g (cluster spin glass transition temperature).

3.2. The spin glass regime $0.02 < x < 0.05$

A variety of measurements have indicated the occurrence of some type of spin glass transition at a temperature $T_g \sim 10$ K in $La_{2-x}Sr_xCuO_4$ for $0.02 < x \lesssim 0.1$ [2]. We have studied this transition via ^{139}La NQR measurements, which exhibit a peak in R_1 at T_g [17]. We find that $T_g \alpha 1/x$ as shown in Fig. 2, in strong contrast to the composition dependence $T_f \alpha x$ for $x < 0.02$ as discussed above. This qualitative difference demonstrates that there is a distinct crossover in the nature of the spin-glass transition at $x \approx 0.02$.

Independent analyses of $T_g(x)$ [14] and $R_1(T)$ [17] indicate that a cluster spin glass is formed at T_g in a collective transition involving freezing of the finite weakly coupled undoped domains discussed above, where the size of the undoped domains in the spin glass regime is found to be $L \propto 1/x^{1/2}$. This $L(x)$ has the same composition dependence as for the 2D AF correlation length ξ in the CuO_2 planes found from inelastic neutron scattering measurements [18], and we identify $L(x) \sim \xi(x)$. The physical picture is then the same as in Section 3.1, in which the doped holes form walls separating weakly coupled undoped domains. In order that the domains be weakly coupled, we expect that the doped holes in the domain walls remain delocalized down to at least T_g, in contrast to the region $x < 0.02$ in which the holes localize below ~ 50 K. Evidently, in the cluster spin glass regime, L is too small, the fluctuations in the local 2D staggered magnetization are too strong, and the intercluster magnetic interactions are too weak, to lead to long-range AF order of the staggered magnetization in the locally ordered undoped 2D domains. The occurrence of a cluster spin glass was predicted theoretically [19,20].

4. CONCLUDING REMARKS

In the $La_2CuO_{4+\delta}$ system, we have determined the structural T-δ phase diagram for $\delta \lesssim 0.1$. A miscibility gap is found between $\delta \approx 0.01$, which is an AF insulator, and $\delta \approx 0.06$, which is a superconductor with $T_c \approx 34$ K. A two-phase region appears to exist between the latter composition and $\delta \approx 0.11$-0.12, which has $T_c \approx 40$-45 K. Thermal-history and time dependent $\chi(T)$ measurements suggest that diffusion of the excess oxygen is significant above ~ 150 K. In the $La_{2-x}Sr_xCuO_{4+\delta}$ system with $\delta \approx 0.03$, the macroscopic phase separation disappears by $x \approx 0.03$. For the $La_{2-x}Sr_xCuO_4$ ($\delta \approx 0$) system in the lightly doped regime with $x \leq 0.05$, evidence was presented that the doped holes form walls separating undoped domains on a nanoscopic length scale. Many of our results support the electronic mechanism for frustrated phase separation in $La_{2-x}Sr_xCuO_4$, and therefore support the same electronic mechanism for macroscopic phase separation in $La_2CuO_{4+\delta}$, which was advanced by Emery and coworkers [20]. An assessment of some of our data in terms of that theory is given in Ref. 20.

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