PHASE SEPARATION AND STAGING BEHAVIOR IN La$_2$CuO$_{4+\delta}$

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Neutron scattering and magnetization measurements have been performed on three single crystals of La$_2$CuO$_{4+\delta}$. For two crystals with $\delta \sim 0.02$ and $0.03$ phase separation of the intercalated oxygen occurs below 280 K whereas stage ordering occurs below 255 K. A third crystal exhibits no phase separation and a higher stage ordering temperature. All three show evidence for an in-plane ordering around 210 K. We propose a phase diagram which summarizes our observations.

Among the family of superconducting copper-oxides, La$_2$CuO$_{4+\delta}$ and La$_{2-x}$Sr$_x$CuO$_4$ have particularly simple structures. La$_2$CuO$_{4+\delta}$ is of great interest because its doping concentration may be well controlled and the oxygen dopants are mobile to temperatures as low as 200 K, in contrast to the quenched disorder resulting from the fixed Sr$^{2+}$ ions in La$_{2-x}$Sr$_x$CuO$_4$. Recent experiments by Wells et al$^1$ have shown that in the oxygen-rich phase of La$_2$CuO$_{4+\delta}$ the oxygen intercalants order into layers parallel to the copper oxide planes. This paper extends the previous work with further experiments on three large single crystals of La$_2$CuO$_{4+\delta}$. In particular, we examine two crystals in the doping regime where phase separation occurs.

Figure 1: Proposed phase diagram for La$_2$CuO$_{4+\delta}$.

The data in this paper together with that from Wells et al$^1$, measured from seven crystals in total, suggest the phase diagram in Figure 1. At low temperatures and low doping, La$_2$CuO$_{4+\delta}$ exhibits three dimensional antiferromagnetic order. For a range of dopings ($\delta \approx 0.012 - 0.055$)$^2,^3$ below room temperature the sample phase separates into oxygen-rich and oxygen-poor phases. In oxygen-rich samples, which are superconducting below $\sim$35 K, the interstitial oxygen dopants order one-dimensionally along the $c$ direction, tending to segregate into planes parallel to the CuO$_2$ layers.
sheets and regularly spaced every \( n \) CuO\(_2\) host layers. We call this configuration stage \( n \), adopting the nomenclature used for intercalated graphite. As we show below, for crystals which phase separate, the phase separation temperature \( T_{PS} \approx 280 \text{ K to } 290 \text{ K} \) is higher than the stage ordering temperature \( T_{SO} \approx 255 \text{ K} \).

All three single crystals used in this experiment were grown at MIT using the travelling-solvent-floating-zone technique. This method does not employ a crucible, hence contamination is reduced, and the crystals appear to be more homogenous than those grown by other means. The crystals are electrochemically oxygenated as described in Ref.1; different oxygen dopings are produced by varying the duration of the electrolysis.

The magnetization, measured with a SQUID magnetometer, at high fields reveals the weak ferromagnetism associated with the antiferromagnetic transition of the undoped phase, as shown in Figure 2(a). From the size of the moment we conclude that the doped crystals are 20% and 45% oxygen-rich by volume. From the phase diagram previously presented by Radaelli et al\(^3\) for powder \( \text{La}_2\text{CuO}_4+\varepsilon \) we infer corresponding macroscopic oxygen concentrations of \( \delta \approx 0.02 \) and \( \delta \approx 0.03 \) respectively. Shielding measurements shown in Figure 2(b) demonstrate that all three doped crystals exhibit Meissner diamagnetism and hence have an oxygen-rich fraction that is superconducting. \( T_c \) for the \( \delta \approx 0.02 \) and 0.03 crystals is about 32 K, while for the crystal labeled stage 4.4, \( T_c \) is about 33 K. It is evident therefore that the two crystals with \( \delta \approx 0.02 \) and 0.03 have at low temperatures a superconducting fraction coexisting with an antiferromagnetic fraction.

![Figure 2: Magnetization of samples as a function of temperature. (a) High field reveals the weak ferromagnetic transition of the oxygen-poor phase. (b) Low field measurements of the shielding signal after slow cooling at zero field. The applied field is along the c direction.](image)

To determine the temperature below which the single crystals phase separate, we performed scans about nuclear Bragg reflections to monitor changes in the lattice constants as a function of temperature. Figure 3(a) shows that at high temperatures there is only one \((0,0,6)\) Bragg peak signifying a single homogenous phase. At low temperature there are two Bragg peaks, corresponding to two different phases with different c-axis lattice constants; the phase with the longer c-axis lattice constant is the oxygen-rich phase and the other is oxygen-poor. The data in Figure 3 are for the \( \delta \approx 0.03 \) sample. The relative intensities of the two peaks at low temperatures provide a second measure of the fractions of sample in the two phases. We find that about 45% of the sample is oxygen-rich, consistent with the magnetization data. From fits to the data, we find that phase separation occurs below \( T_{PS} \approx 290 \text{ K} \). This is a lower phase separation temperature than that for the powder samples as studied by Radaelli et al\(^3\) The \( \delta \approx 0.02 \) sample also phase separates with \( T_{PS} \approx 280 \text{ K} \). However, the stage 4.4 sample does not phase separate signifying that it is doped beyond the miscibility gap.
Figure 3: Crystal with $\delta \sim 0.03$, about 45% oxygen-rich. (a) Scans over a fundamental nuclear Bragg peak. (b) Temperature dependence of the lattice constants obtained from scans like those in (a).

A range of staging numbers from $n = 2$ to 7 have been observed in La$_2$CuO$_{4+\delta}$. Staging is evidenced by incommensurate peaks displaced along $L$ on either side of the Bmab superlattice peaks which originate from the tilting of the CuO$_6$ octahedra in the orthorhombic phase. In a homogenous staged sample, the commensurate Bmab superlattice peaks disappear altogether being replaced by the two incommensurate peaks. These staging superstructure peaks result from antiphase domain boundaries at which the CuO$_6$ octahedra tilt direction reverses. This reversal is presumed to be caused by the intercalated oxygen layers, similar to the model proposed by Tranquada et al. for La$_2$NiO$_{4+\delta}$. For the two samples doped in the miscibility gap, we find that the oxygen-rich phase has $n = 6.3$ at low temperatures. For the sample that was doped beyond the miscibility gap, we find that $n = 4.4$, independent of temperature. This suggests that $n$ is simply a function of the amount of oxygen in the oxygen-rich phase.

Figure 4 presents data taken on the $\delta \sim 0.02$ sample. The temperature dependence of the lattice constants in the top panel of part (a) shows phase separation occurring below $T_{PS} \simeq 280$ K. The lower panel shows the temperature dependence of the 2D integrated intensity in the $(0,K,L)$ plane of the $(0,1,4.15)$ staging peak from fits to a 2D gaussian. We see that the onset of stage ordering in this sample occurs at $T_{SO} \simeq 255$ K. The staging number evolves from $\sim 7.1$ to 6.3 with decreasing temperature. The sample with $\delta \sim 0.03$ follows the same behavior. Examining the staging intensity upon slow cooling and slow warming (220 K to 260 K in 25 hours), we find 5 K hysteresis. In the stage 4.4 sample, stage ordering occurs at a higher $T_{SO} \simeq 290$ K. However the sample remains orthorhombic, and there is no commensurate Bmab superlattice peak up to at least 330 K, suggesting that above 290 K the tilts are disordered.

An apparent drop in the intensity of the staging peak occurs for temperatures below 210 K, as first reported by X. Xiong et al. This results from the establishment of an in-plane modulation, in which the staging peak itself splits into two superlattice peaks along $H$. Scans along $H$ through the $(0,1,4.15)$ staging peak are shown in Figure 4(b) taken on warming. From the width of the single staging peak at 220 K, we estimate a staging domain size of about 83 lattice constants along $a$. As the crystal cools, the staging peak intensity diminishes and two peaks rise on either side. The two
Figure 4: Crystal with $\delta \sim 0.02$, about 20% oxygen-rich. (a) The upper panel shows the temperature dependence of the lattice constants; the lower panel shows the temperature dependence of the 2D integrated intensity of the (0,1,4.15) staging peak. (b) Scans along H through the (0,1,4.15) staging peak. The solid line for the 220 K and 210 K scans is a fit to a lorentzian convolved with the resolution function. Note the change of scale for the vertical axis. The solid line for the lower temperature scans is a fit to three 3D gaussians.

new peaks appear in coexistence with the initial staging peak, implying a first-order transition. The displacement of the superlattice peaks from the original staging peak position suggests that they are caused by a modulation along H with a periodicity of about 11.5 a. Thus, this in-plane ordering occurs within a staging domain. No new satellite peaks are found along the in-plane K direction. A similar drop in staging peak intensity is seen in the $\delta \sim 0.03$ sample and, to a much lesser extent, in the stage 4.4 sample, suggesting that this H modulation also occurs in these crystals.

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