Direct Observation of Incommensurate Modulation in Phase-Separated Cu-Rich $La_2CuO_{4.003}$

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An incommensurate modulation was observed directly for the first time by transmission electron microscopy in a phase-separated Cu-rich $La_2CuO_{4.003}$ crystal at room temperature and at 93 K. After annealing in Ar atmosphere, both incommensurate modulation and phase separation disappeared. It is concluded that the incommensurate modulation is attributed to the phase separation, while the occurrence of phase separation in the sample with such a low excess oxygen content results from the enhanced antiferromagnetic interaction due to the Cu dopant. [S0031-9007(98)05519-7]

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The high transition temperature (high-T_c) superconductors based on the structure with square-planar copper-oxide layers are derived from the antiferromagnetic insulators. The undoped parent compound has one unpaired $3d$ electron with spin of $\frac{1}{2}$ for each copper ion. Below Néel temperature T_N, these spins align into three-dimensional long range antiferromagnetic order [1]. In recent years, extensive attention has been focused on the doping behavior of antiferromagnetic parent compounds. Consequently, La_2CuO_4 has attracted considerable interests, because it is the material that possesses the simple and typical structure among high-T_c superconductors and very possibly exhibits the desired physical properties upon doping. Two methods are usually employed to achieve the hole doping for the La_2CuO_4 superconductor. One is to replace the La^{3+} ions partially by cations with 2^+ valence (M^{2+}), such as in $La_{2-x}Sr_xCuO_4$ [2] and $La_{2-x}Ca_xCuO_4$ [3], etc.; another method is to intercalate excess oxygen into interstitial sites to create holes in the Cu-O plane of the La_2CuO_4 system [4]. In the underdoping level, the holes created in the Cu-O plane of $La_2CuO_{4+\delta}$ partially destroy the long range antiferromagnetic order; meanwhile, the superconducting phase arouses in the background of the long range order antiferromagnet. Because of the mobility of oxygen dopant, the $La_2CuO_{4+\delta}$ more easily tends to phase separate into hole-rich and hole-poor regions than the case of cation doping [5,6]. The coexistence of superconducting phase and antiferromagnetic phase is one characteristic feature of phase separation. The phenomenon of phase separation occurring in the range from $\delta \approx 0.01$ to 0.055 in $La_2CuO_{4+\delta}$ has been extensively explored [5,6], whereas no phase separation has been reported for the region with $\delta < 0.01$.

Recently, stripe phase [7] in *ab* plane of the $La_2CuO_{4+\delta}$ system was observed when the oxygen doping content is well beyond the phase separation range. This stripe phase was suggested to be closely associated with oxygen doping. In addition, this kind of stripe was also observed in Nd and Sr doped systems such as $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ [8] and $La_{1.85}Sr_{0.15}CuO_4$ [9]. The stripe direction was observed, however, to be very different from that observed in the La_2NiO_4 system [10]. This difference, which was attributed to the considerable dissimilar properties between these two systems, was suggested to be decisive for the occurrence of superconductivity in the copper-oxide compound instead of the nickel-oxide one [11,12].

According to the knowledge of the important role of Cu-O plane on high-T_c superconductivity and the fact that different stripes were observed in La_2CuO_4 and La_2NiO_4, the role of the copper content on phase separation and structural features should be taken into consideration for understanding the mechanism of phase separation. It was suggested that the excess Cu^{2+} ion with a spin of $\frac{1}{2}$ might enhance the two- and three-dimensional antiferromagnetic exchange interaction by possibly substituting the La site with Cu, hence promoting phase separation by driving the holes to segregate [13]. The purpose of the present work is to make a further investigation on the effects of excess Cu for phase separation, mainly on the microstructure feature of the Cu-rich $La_2CuO_{4+\delta}$.

The La-Cu-O powder samples were prepared using the conventional solid state reaction method, including a powder mixing technique and a sintering process, which were described in detail previously [14]. The composition of La:Cu = 2:1.06 (atomic ratio) was selected for studying the influence of excess copper on phase separation, since the value of excess copper, 0.06, is large enough to show the influence of excess copper on phase separation, and the sample with such a value of excess copper, according to the step x-ray analysis reported elsewhere [13], still reveals single phase though its lattice shrinks

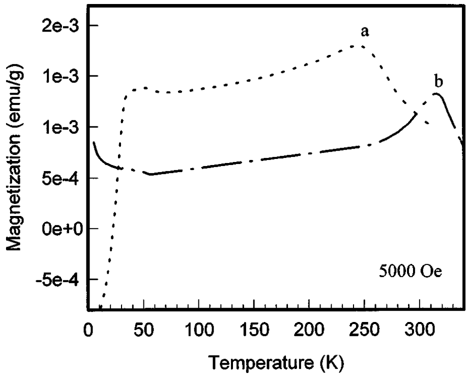

FIG. 1. Magnetization versus temperature for the Cu-rich $La_2CuO_{4.003}$ sample: (*a*) as-prepared, and (*b*) Ar annealed.

by contrast with that of a stoichiometric one. The excess oxygen value of this sample, $\delta = 0.003$, was determined from the gas effusion spectra method. The gas effusion experiment is performed by continuously heating the sample in a sealed quartz tube under vacuum and recording the total gas pressure as a function of temperature; thus the δ value can be calculated from the change of gas pressure caused by the effusion of excess oxygen in the sample [15]. The phase separation was revealed by magnetization measurements which were carried out using Quantum Design MPMS-5 equipment with an applied magnetic field of 5000 Oe. While for the sample with La:Cu = 2:1 prepared by the same procedure, no phase separation was detected [14]. Transmission electron microscopy (TEM) observations were performed by using a Philips CM200/FEG with a liquid nitrogen Gatan cooling double-tilt stage.

The magnetization versus temperature curves of the Cu-rich $La_2CuO_{4.003}$ sample measured for the cases both before and after Ar-flow annealing (at 800 °C for 8 h) are plotted in Fig. 1. It is clearly shown that the superconducting phase with $T_c \sim 35$ K coexists with the antiferromagnetic phase with the Néel temperature $T_N \sim 244$ K before annealing (curve *a*). After annealing in the flowing Ar gas at 800 °C for 8 h, the superconductivity of the sample disappeared and the Néel temperature arose up to ~ 320 K (curve *b*) since almost all of the excess oxygen atoms in the sample are extracted. This apparently indicates that the occurrences of phase separation as well as superconductivity in the Cu-rich $La_2CuO_{4.003}$ sample are caused by excess oxygen doping. But, taking the experimental fact in the previous experiments [14] into account, that the phase separation was not detected from the magnetization measurements for sample L1 ($La_2CuO_{4+\delta}$ with La:Cu = 2:1) prepared by the same procedure, the influence of excess copper on phase separation cannot be ignored. In addition, one fact worth noting is that after the same annealing treatment the sample of La_2CuO_4 with La:Cu = 2:1 shows a Néel temperature of 295 K, 25 K lower than that of Cu-rich La_2CuO_4, 320 K. This should be direct evidence that the antiferromagnetic interaction in Cu-rich La_2CuO_4 is stronger than that in La_2CuO_4.

Figure 2(a) is a [100] zone axis high resolution electron microscopy image (HREM) of the Cu-rich $La_2CuO_{4.003}$ sample at room temperature. The inset shows the Fourier transform of the image. Stripelike structure with a period of about 1.9 nm is observed for the first time at room temperature. The selected area electron diffraction pattern from the same area is shown in Fig. 2(b), from which an incommensurate modulation structure with a vector q of $0.192b^* + (1/2)c^*$ is identified, this corresponds to the stripe structure in Fig. 2(a). Previous experimental observations indicated that, due to the mobility of the doped interstitial oxygen, the ordering structure in the $La_2CuO_{4+\delta}$ system with enough excess oxygen content could only be identified below 200 K [7–9,16]. In addition, no ordering structure has yet been reported in $La_2CuO_{4+\delta}$ when the excess oxygen $\delta < 0.03$. Now, in the Cu-rich case, an incommensurate modulation structure can be identified at room temperature quite clearly with such a small excess oxygen content of $\delta = 0.003$.

Figure 3 is a [100] zone axis electron diffraction pattern taken at 93 K. The incommensurate modulation becomes more evident than that observed at room temperature, and the vector q changes to $0.246b^* + (1/3)c^*$. This vector is very close to that $q = 0.21b^* + (1/3)c^*$ observed in the $La_2CuO_{4.1}$ single crystal below 150 K [7], whereas

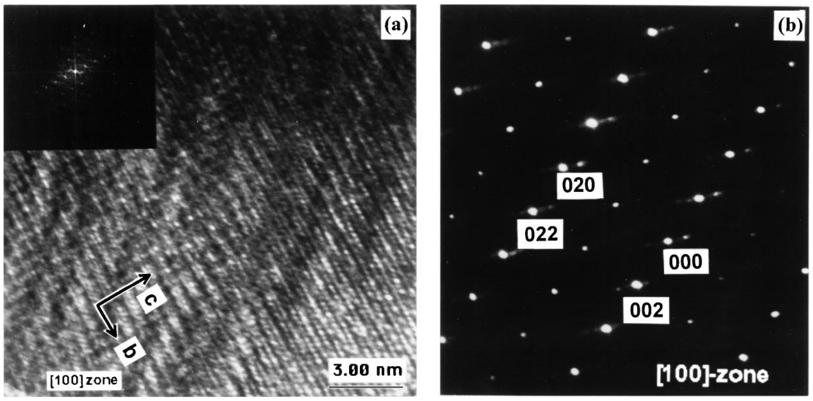

FIG. 2. (a) The [100] zone axis HREM image of the Cu-rich $La_2CuO_{4.003}$ sample at room temperature. (b) The selected area electron diffraction pattern corresponding to (a).

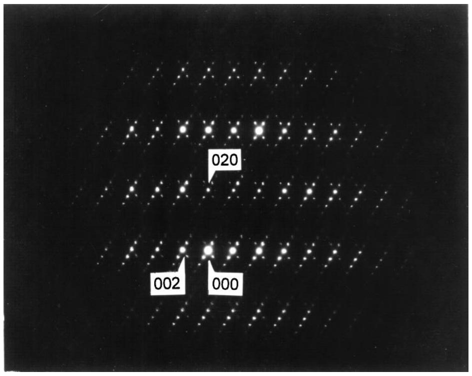

FIG. 3. The [100] zone axis electron diffraction pattern for the as-prepared sample at 93 K.

the period remains approximately the same as 1.9 nm. In order to understand the origin of this stripe structure, TEM observations were also carried out for the Ar-annealed Cu-rich La_2CuO_4 sample. Figure 4(a) is a [100] zone axis HREM image of the Ar-annealed Cu-rich La_2CuO_4 sample, and Fig. 4(b) is the corresponding electron diffraction pattern. The results showed that no stripe structure was visible. This indicates that the formation of incommensurate modulation is related to the phase separation associated with the excess oxygen (i.e., related to the doped holes), and apparently is a character of charge ordering.

According to Emery *et al.* [11], the charge stripes together with antiphase spin domains are expected on the CuO_2 planes as a competition between the long range part of the Coulomb interaction and the tendency toward phase separation. In the present case, this kind of competition might also take effect along the c axis due to the enhancement of three-dimensional antiferromagnetic exchange interaction caused by excess copper. Hence, the appearance of incommensurate modulation about the c axis is understandable. Of course, the mechanism of formation of this kind of incommensurate modulation needs to be investigated further.

So far, we may conclude that the excess copper in the $La_2CuO_{4+\delta}$ system can greatly promote phase separation by enhancing the antiferromagnetic exchange interaction. The promoted phase separation is characterized by its appearance in the sample with excess oxygen as small as $\delta = 0.003$. As indicated experimentally and theoretically in the $La_2CuO_{4+\delta}$ system [11,16], mobile holes will tend to form an ordered state (charge ordering) when their concentration reaches a certain value, and the incommensurate modulation thereby forms. The enhanced antiferromagnetic exchange interaction due to the excess copper tends to force the holes to segregate; in consequence, the necessary hole concentration for superconductivity can be achieved in some local areas even if the average excess oxygen content of the sample is very small. After annealing in Ar atmosphere, holes introduced by excess oxygen are removed; therefore, both phase separation and incommensurate modulation disappear as expected.

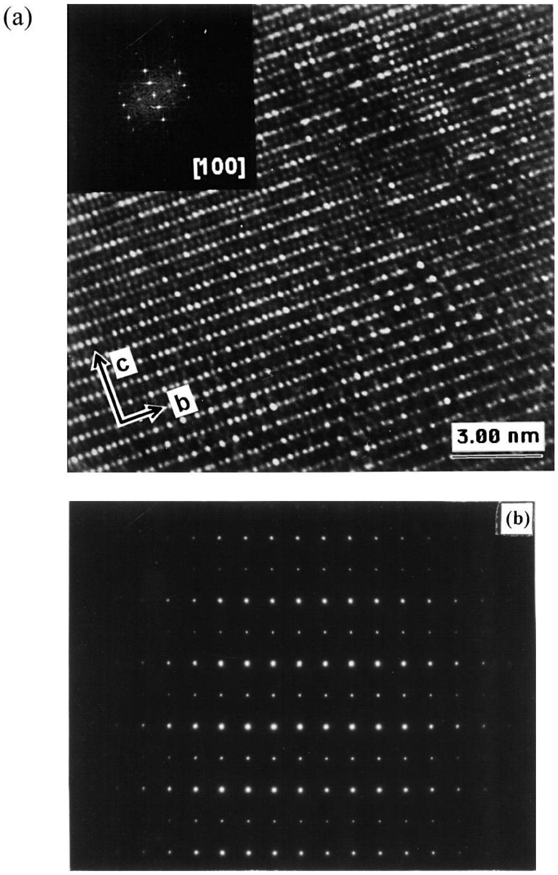

FIG. 4. (a) The [100] zone axis HREM image of the Ar-annealed Cu-rich La_2CuO_4 sample at room temperature; the inset is the Fourier transform. (b) The selected area electron diffraction pattern corresponding to (a).

Furthermore, it has been suggested that the diffusion of single hole cluster is space limited at $150 \leq T \leq 170$ K and space unrestricted above 180 K in the La_2CuO_4 system [17], implying that the charge ordering will appear only below 180 K in the usual $La_2CuO_{4+\delta}$ samples. This limitation is expected to depend on the competition between the antiferromagnetic exchange interaction and the thermal fluctuation. The former forces the holes to segregate and form an ordering state in the hole-rich region, while the latter prefers a random hole distribution in the whole sample. The enhanced antiferromagnetic exchange interaction due to the excess copper will therefore raise the phase separation temperature and consequently elevate the upper limit of charge-ordering temperature. The incommensurate modulation structure observed at room temperature can therefore be understood. At relatively lower temperature, the thermal fluctuation will become weak; this will benefit the charge ordering. As a result, the incommensurate modulation becomes strong when the temperature is lowered.

In summary, we have for the first time observed an incommensurate modulation, which is a kind of charge ordering, at room temperature in the Cu-rich $La_2CuO_{4.003}$ single-phased sample (La:Cu = 2:1.06), and found that the modulation wave vector changed slightly when the temperature was decreased from room temperature to 93 K. The excess copper can promote phase separation greatly; hence, remarkable features of the microstructure are generated though the excess oxygen content is as small as 0.003. Our observations were interpreted based on the enhancement of antiferromagnetic exchange interaction due to the Cu dopant, and the results imply that the mechanism of phase separation may be studied in relatively wide temperature and doping ranges.

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