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The effects of interstitial oxygen on superconducting electronic phases in strontium and oxygen co-doped $La_{1.937}Sr_{0.063}CuO_{4+\delta}$*

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Strontium and oxygen co-doped $La_{1.937}Sr_{0.063}CuO_{4+\delta}$ superconductor with $T_c \approx 40$ K, which is obtained by oxidizing strontium-doped starting ceramic sample $La_{1.937}Sr_{0.063}CuO_4$ in NaClO solution, is annealed under different conditions to allow interstitial oxygen to redistribute. The evolution of the intrinsic superconducting property with the oxygen redistribution is studied in detail by magnetic measurements in various fields. It is found that there occurs the electronic phase separation from the single superconducting phase with $T_c \approx 40$ K into two coexisting superconducting states with values of T_c: 15 and 40 K or of 15 and 35 K in this system, depending on annealing condition. Our results indicate that the 15, 35 and 40 K superconducting phases associated with the excess oxygen redistribution are all thermodynamically meta-stable intrinsic states in this Sr/O co-doped cuprate.

Keywords: $La_{2-x}Sr_xCuO_4$, intrinsic electronic phase, interstitial oxygen
PACC: 7430C, 7470S

1. Introduction

The La_2CuO_4 (La-214) family is a simple and good model system in studying the mechanism of high temperature superconductivity, which manifests many interesting and important physical properties such as phase separation,[1−4] microscopic electronic inhomogeneity,[5,6] complex charge orderings including stripes,[7,8] two-dimensional Wigner charge lattice[9] and checkboard charge ordering.[10−12] The antiferromagnetic parent La_2CuO_4 can be transformed into superconductor by cation (e.g. Sr^{2+}, Ba^{2+}) doping and anion (e.g. O^{2-}) doping. In this system, the cationic dopants occupy lattice sites and are immobile due to large Madelung potentials at lattice sites. Anionic doping, however, frequently results in a system of mobile dopants (i.e. interstitial oxygens in La-214 system) that provide an additional degree of freedom and may respond to a change of thermodynamic parameters such as temperature and pressure. For example, the hydrostatic pressure up to 2 GPa at room temperature can cause a redistribution of holes in Sr/O co-doped $La_{2-x}Sr_xCuO_{4+\delta}$.[4]

Since the discovery of superconductivity in $La_{2-x}Sr_xCuO_4$ (LSCO), many studies have been carried out on the effects of varying the cationic substitution of Sr^{2+} for La^{3+} and the oxygen stoichiometry. It was reported that there was an intrinsic tendency of electronic phase separation of doped holes into distinct superconducting states in Sr/O co-doped $La_{2-x}Sr_xCuO_{4+\delta}$.[4] Recently, our further detailed magnetic analysis of high-quality crystal samples has evidenced that there exist two intrinsic superconducting states with values of T_c of 15 and 30 K at the magic doping levels of $x = 1/16$ (0.0625) and 1/9 (≈ 0.11), respectively, in the underdoping regime of strontium doped $La_{2-x}Sr_xCuO_4$.[13,14] A robust T_c in magnetic fields up to 5 Tesla is one of the characteristics of the thermodynamically meta-stable intrinsic superconducting phase, which is distinct from the superconducting phase away from the magic dopings whose T_c can be easily reduced by a field above 0.1 T. In order to examine the response of intrinsic electronic property to the variation in charge doping

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near the magic concentration of $x = 1/16$, we annealed $La_{1.937}Sr_{0.063}CuO_4$ crystal under various conditions to moderately adjust the oxygen content and studied the intrinsic superconducting property.[15] The doping of $x = 1/16$ is special in that a $4a \times 4a$ square lattice charge ordering has been proposed to preferentially form at this doping level[9] which has also been theoretically discussed.[11,16] The excess oxygen content doped into this crystal sample by annealing was found to be limited even it was done under higher oxygen pressures. Our results showed that a moderate change in oxygen doping did not significantly modify the intrinsic electronic state in the $La_{1.937}Sr_{0.063}CuO_4$ crystal, indicating there was a tolerant region around the magic doping for intrinsic electronic state.[15] A consequent interesting issue for us is thus to further study the response of intrinsic electronic state to a larger change in oxygen doping in this cuprate. For this purpose, in this work we select a different route to increase oxygen doping efficiency in the cuprate. In order to compare with our previous results of $La_{1.937}Sr_{0.063}CuO_4$ crystal,[14,15] we first synthesize a $La_{1.937}Sr_{0.063}CuO_4$ ceramic sample then oxidize it in NaClO solution, which gives high oxidation efficiency. The as-prepared Sr/O co-doped sample with high oxygen doping is annealed under different conditions and the effect of interstitial oxygen redistribution on intrinsic superconducting property is studied in detail by magnetic measurements in various magnetic fields.

2. Experiment

The starting ceramic sample of strontium doped $La_{1.937}Sr_{0.063}CuO_4$ was synthesized by the conventional solid-state reaction route using stoichiometric amounts of La_2O_3, $SrCO_3$ and CuO powders with a purity of 99.99%. La_2O_3 powder was calcined at 850°C for 8 h before weighing. The starting materials were mixed thoroughly and calcined at 925°C for 40 h followed by heating at 980°C again for 40 h with intermediate grindings. The product was reground and pressed into pellets before sintered at 1000°C for 40 h and cooled at a rate of 30°C/h to room temperature in air. Note that the oxygen stoichiometry of the as-prepared ceramic sample could slightly exceed 4; it is designated as 410 cm this paper for simplicity.

The chemical oxidation of the as-prepared $La_{1.937}Sr_{0.063}CuO_4$ ceramic powder was performed using the following methods: about 4 g of the $La_{1.937}Sr_{0.063}CuO_4$ powder was dissolved into NaClO aqueous solution to be oxidized at room temperature for 13 d. The NaClO solution containing $La_{1.937}Sr_{0.063}CuO_4$ powder was stirred periodically in order to assure uniform intercalation of excess oxygen. The aqueous solution of NaClO is volatile and was re-added frequently. After the oxidation treatment, the powder was filtered, washed with distilled water and ethanol, and dried in silica gel desiccator at room temperature. Thus fully oxidized Sr/O co-doped compound $La_{1.937}Sr_{0.063}CuO_{4+\delta}$ (called oxidized LSCO in this paper) was pressed into pellets each with a diameter of 5 mm. The material was then annealed at 100°C and 200°C in air in different time lengths followed by quenching to room temperature to adjust the interstitial oxygen distribution.

X-ray powder diffraction was performed on M18XHF diffractometer using Cu K_α radiation. The magnetic measurements of the samples were carried out on a Quantum Design SQUID magnetometer (MPMS-XL1). The magnetization was always measured after field-cooled and during warming cycles and the sample was always positioned at the centre of the detecting coil during cooling and adjusting field for minimizing the flux trapping.

3. Results and discussion

Shown in Fig.1 are the powder x-ray diffraction patterns for all our samples: strontium doped starting ceramic LSCO sample, Sr/O co-doped oxidized LSCO,

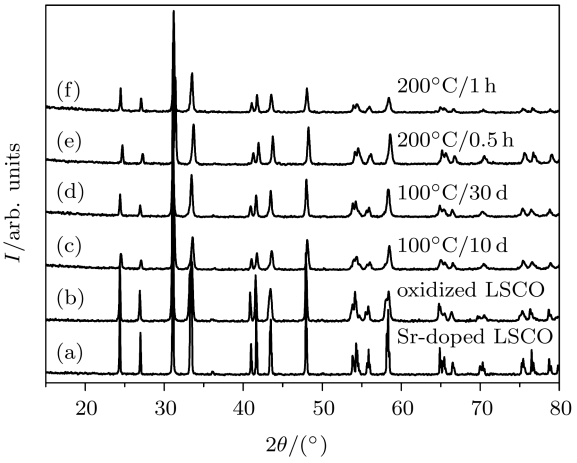


Fig.1. The powder x-ray diffraction patterns for all our samples: (a) strontium doped starting ceramic LSCO sample; (b) Sr/O co-doped oxidized LSCO; (c) and (d) oxidized LSCO annealed at 100°C for 10 and 30 d respectively; (e) and (f) oxidized LSCO annealed at 200°C for 0.5 and 1 h respectively.

oxidized LSCO annealed at 100°C for 10 and 30 d and that annealed at 200°C for 0.5 and 1 h. All the diffraction patterns are characteristic of the same La-214 structure and no impurity phase is detected. The lattice parameters calculated from the XRD data are $a \approx 0.5368$ nm, $b \approx 0.5347$ nm and $c \approx 1.3185$ nm for starting ceramic LSCO sample. After oxidation, a and c increase, respectively, to 0.5388 nm and 1.3232 nm while b decreases to 0.5340 nm for oxidized LSCO. The cell parameters do not vary much after annealing, with $a \approx 0.5379$ nm, $b \approx 0.5353$ nm and $c \approx 1.3199$ nm for the sample annealed at 200°C for 1 h. Figure 2 is the thermogravimetry analysis (TGA) of $La_{1.937}Sr_{0.063}CuO_{4+\delta}$ sample fully oxidized in NaClO for 13 d. The excess oxygen content of the sample, δ, is estimated from the TGA data to be about 0.118.

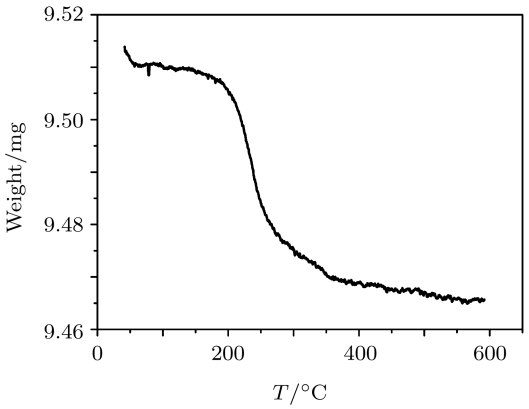


Fig.2. The TGA curve of $La_{1.937}Sr_{0.063}CuO_{4+\delta}$ sample fully oxidized in NaClO for 13 d, measured in air at a scan rate of 10°C/min.

Plotted in Figs.3 and 4 are the temperature dependences of magnetic susceptibility in the superconducting transition region (Figs.3(a) and 4(a)), and its differential quotient with respect to temperature, $d\chi/dT$ (Figs.3(b) and 4(b)), under a field of 5×10^{-4} T for oxidized LSCO and those annealed at 100°C for 10 and 30 d and at 200°C for 0.5 and 1 h, respectively. Each $d\chi/dT$ curve is arbitrarily shifted vertically for clarity. For the oxidized LSCO sample, a single superconducting transition occurs at about 40 K (the superconducting transition temperature T_c is defined as the temperature at which the diamagnetic transition just occurs). This is clearly indicated by the single peak in its differential curve (Figs.3(b) and 4(b)). After the oxidized LSCO has been annealed at 100°C for 10 and 30 d, a second superconducting transition appears at about 15 K besides the original 40 K one, which can be clearly seen from the broadened and structured

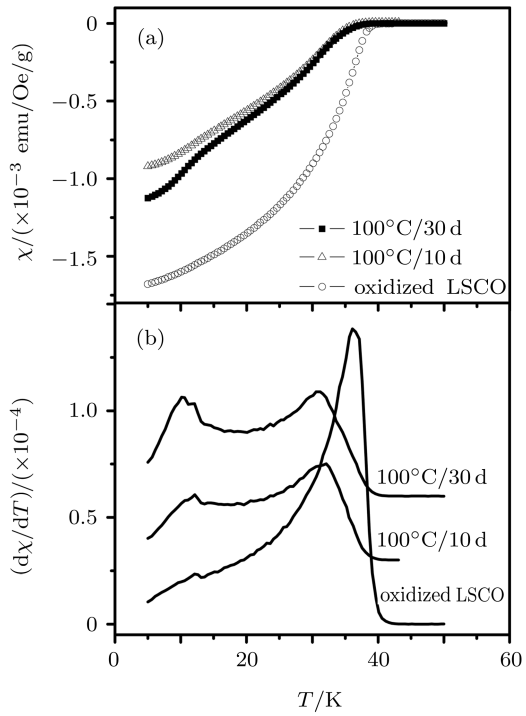


Fig.3. Temperature dependences of magnetic susceptibility in the superconducting transition region (a), and the corresponding differential quotients with respect to temperature $d\chi/dT$ (b) for the oxidized LSCO and that annealed at 100°C for 10 and 30 d. 1 Ce = 79.5775 A/m.

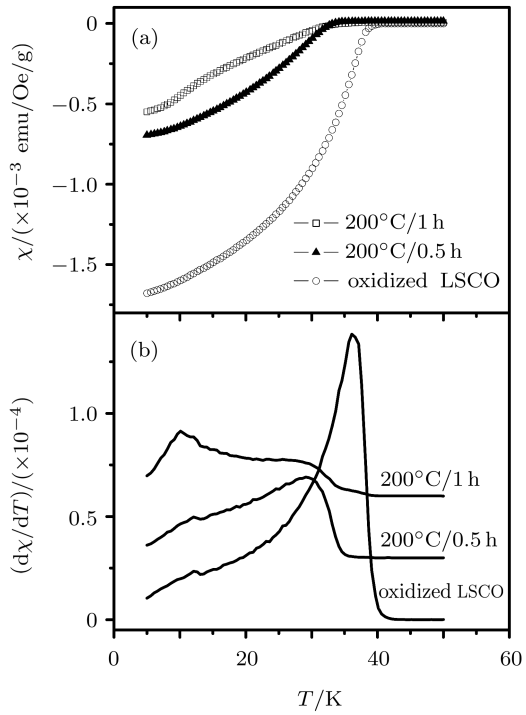


Fig.4. Temperature dependences of magnetic susceptibility in the superconducting transition region (a), and the corresponding differential quotients with respect to temperature $d\chi/dT$ (b) for the oxidized LSCO and that annealed at 200°C for 0.5 and 1 h. 1 Oe = 79.5775 A/m.

differential curves. Furthermore, this 15 K superconducting phase seems to be enhanced when the annealing time increases from 10 d to 30 d. This phenomenon indicates that with the annealing process the cuprate system tends to separate the phase into two superconducting states. It was reported[17] that the La-214 system did not lose interstitial oxygen at temperatures below 110°C. Our TGA data for oxidized LSCO (Fig.2) also shows that there is no mass loss at 100°C. Hence, the oxygen loss in oxidized LSCO annealed at 100°C can be neglected. Although the global charge carrier number remains unchanged, the annealing at 100°C can cause the redistribution of mobile interstitial oxygen in the oxidized LSCO. According to the previously proposed composite charge model,[18] the free or superfluid electrons innately coexist with underlying 2D charge lattice orderings in CuO_2 planes. When the mobile oxygens rearrange themselves into energetically favourable states with the annealing, the distinct thermodynamically metastable domains of charge ordering or charge inhomogeneity may be formed. In this sense, this superconducting phase separation occurring with the annealing process may be understood as being associated with the formation of specific charge orderings due to the chemical phase separation of interstitial oxygens.

When the oxidized LSCO is annealed at 200°C, an oxygen loss will occur according to the TGA curve given in Fig.2. Consequently, the superconducting transition temperature T_c of the oxidized LSCO annealed at 200°C for 0.5 h drops from 40 to 35 K, accompanied by a broadening in the transition as shown in Figs.4(a) and 4(b). It can also be seen from Figs.4(a) and 4(b) that after the annealing time has increased to 1 h, a second superconducting phase with $T_c \approx 15$ K can again be detected from the broadened transition curves in addition to the 35 K one, which is similar to the case shown in Fig.3. At the present case, due to a decrease in the total hole concentration, the redistribution of excess oxygen causes the original 40 K superconducting phase to be separated into two distinct superconducting phases separately with values of T_c of 35 K and 15 K.

Given in Figs.5–7 are the differential curves of $d\chi/dT$ in various magnetic fields for the annealed oxidized LSCO. It can be seen that the values of T_c of 40 and 35 K for the oxidized LSCO annealed at 100°C and 200°C, respectively, remain unchanged with the increase of magnetic field. As we mentioned above, this robust T_c in a magnetic field is characteristic

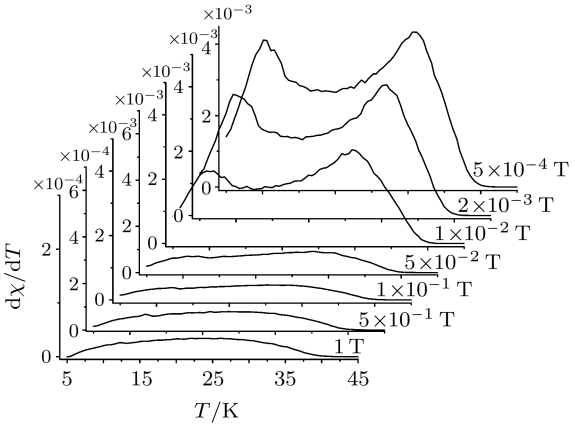


Fig.5. The temperature dependences of $d\chi/dT$ in various magnetic fields for the oxidized LSCO annealed at 100°C for 30 d.

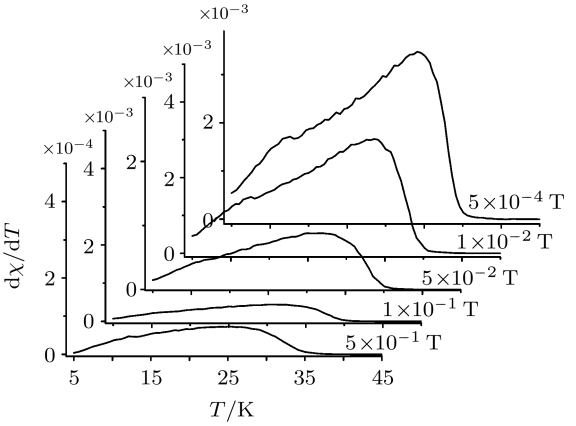


Fig.6. The temperature dependences of $d\chi/dT$ in various magnetic fields for the oxidized LSCO annealed at 200°C for 0.5 h.

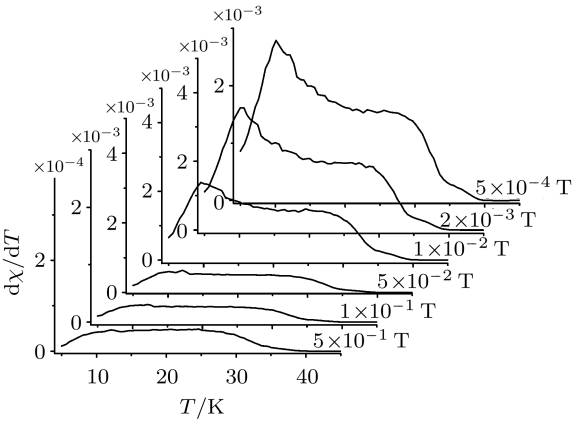


Fig.7. The temperature dependences of $d\chi/dT$ in various magnetic fields for the oxidized LSCO annealed at 200°C for 1 h.

of the intrinsic superconducting state. For the oxidized LSCO annealed at 100°C for 30 d and at 200°C for 1 h (Figs.5 and 7), the signal of 15 K superconducting phase clearly detected at lower fields gradually merges into the broad background of the $d\chi/dT$

curves with field increasing. However, the behaviour of their $d\chi/dT$ curves can be distinguished from that for the case of annealing at 200°C for 0.5 h in which no 15 K superconducting signal is detected and the $d\chi/dT$ curve drops rapidly at lower temperatures as shown in Fig.6. This difference implies that there still remains the contribution of 15 K superconducting phase at higher fields in the former two samples.

4. Conclusion

Strontium and oxygen co-doped $La_{1.937}Sr_{0.063}CuO_{4+\delta}$ superconductor is prepared by oxidizing the strontium-doped starting ceramic sample $La_{1.937}Sr_{0.063}CuO_4$ in NaClO solution. The excess oxygen content, δ, is estimated by TGA analysis to be about 0.118. The as-prepared Sr/O co-doped LSCO exhibits a single superconducting transition at $T_c = 40$ K. When the co-doped LSCO is annealed at 100°C for 30 d and at 200°C for 1 h, it clearly occurs that the electronic phase is separated from the single superconducting phase of $T_c = 40$ K into two coexisting superconducting phases with the values of T_c: about 40 and 15 K or about 35 and 15 K, respectively. In the former case, the electronic phase separation is related to a pure redistribution of interstitial oxygens without oxygen loss in the cuprate, and in the latter case there occurs an oxygen loss together with the redistribution of oxygens so that the value of T_c drops from 40 to 35 K. Furthermore, it is proposed that the redistribution of excess oxygens may be beneficial to the formation of specific charge ordering domains. Our experiments indicate that the superconducting phases with the values of T_c: 40, 35 and 15 K, which are associated with the oxygen redistribution, are all thermodynamically meta-stable intrinsic states in this Sr/O co-doped cuprate. Finally, due to the mobility of interstitial oxygen, high oxygen doping can cause dramatic changes in intrinsic electronic state in this cuprate, this is in contrast with the result in our another work on $La_{1.937}Sr_{0.063}CuO_4$ crystal[15] where oxygen content was only moderately adjusted and the intrinsic electronic state was not significantly influenced.

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