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Effect of heat treatment on electronic phase in underdoped $La_{2-x}Sr_xCuO_4$ single crystal*

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Superconducting $La_{1.937}Sr_{0.063}CuO_4$ crystals grown by the travelling-solvent floating-zone technique were thermally treated under various temperatures and oxygen pressures for moderately adjusting the oxygen content. The response of intrinsic electronic property of the crystals to the change of hole density in $La_{2-x}Sr_xCuO_4$ in the vicinity of the magic doping of $x = 1/16$ (= 0.0625) is studied in detail by magnetic measurements under various fields up to 1 T. It is found that when the superconducting critical temperature (T_C) increases with the oxygen content, there appears also a new subtle electronic state that can be detected from the differential curves of diamagnetic susceptibility $d\chi/dT$ of the crystal sample. In contrast with the intrinsic state, the new subtle electronic state is very fragile under the magnetic fields. Our results indicate that a moderate change in oxygen doping does not significantly modify the intrinsic electronic state originally existing at the magic doping level.

Keywords: $La_{2-x}Sr_xCuO_4$, single crystal, superconductive electronic phase
PACC: 7430C, 7470V

1. Introduction

High-temperature cuprate superconductors $La_{2-x}Sr_xCuO_4$ (LSCO) can be produced by carrier doping into the Mott insulator parent material La_2CuO_4 with strongly correlated electrons. Quite different from electronically uniform conventional superconductor, electronic inhomogeneity[1,2] and phase separation[3−6] were found to be common features in cuprate superconductors. Various electronic inhomogeneities such as stripes,[7,8] two-dimensional Wigner charge lattice[9] and checkboard charge ordering[10−13] in the CuO_2 plane have been proposed and studied. Recent experiments have revealed that there exist robust intrinsic superconducting phases with $T_C = 15$ and 30 K in the vicinity of specific 'magic' doping level $x = 1/16$ (= 0.0625) and 1/9 (= 0.111), respectively, where two-dimensional (2D) charge lattice with specific symmetry is expected, in underdoped LSCO crystals.[14] Clearly, the interplay of doping level, charge ordering and high-T_C superconductivity is an important topic in understanding the origin of high-T_C superconductivity.

Introducing charge carrier into the La_2CuO_4 system is usually achieved in two ways: cation (such as Sr^{2+}) doping and anion oxygen doping. Extensive studies have been performed on the superconducting properties of the Sr/O co-doped $La_{2-x}Sr_xCuO_{4+\delta}$ ceramic samples.[5,15,16] As one of our serial studies on intrinsic electronic states in cuprate superconductor crystals,[14,17,18] the aim of the present work is to examine the response of intrinsic electronic property to the charge doping in underdoped LSCO crystals through a moderate adjustment of charge density around the magic doping level. In order that the experimental results obtained are more reliable, we choose to anneal the same as-grown LSCO crystal with a strontium doping level fixed near the magic doping of $x = 1/16$ under various temperatures and oxygen pressures to moderately change the oxygen content, and all the measurements are carried out on the same sample. The reason we choose the LSCO crystal with strontium doping x of about 1/16 is that the oxygen can be much easier intercalated into a LSCO structure with lower strontium doping, and a $4a \times 4a$ square lattice charge ordering has been proposed to preferen-

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tially form at the specific doping level $x = 1/16$,[9] which has also been discussed theoretically.[11,13,19] The electronic behaviours of the thermally treated crystal sample under various magnetic fields up to 1 T are also studied in detail in this work.

2. Experimental details

The single crystal of $La_{1.937}Sr_{0.063}CuO_4$ was grown by the travelling-solvent floating-zone technique. Details of the crystal growth were reported in our previous papers.[17,18] The crystallographic orientation of the sample was determined by the x-ray Laue analysis. From the crystal a rectangular thin platelet with a mass of 12.45 mg and a size of $2.44 \times 1.12 \times 0.8\,mm^3$ was cut, with the c-axis perpendicular to the biggest face. The as-grown $La_{1.937}Sr_{0.063}CuO_4$ crystal was thermally treated under various temperatures (ranging from 500 to 900°C) and oxygen pressures (from 2×10^5 to 2×10^6 Pa) for 105-360 hours. In the end of each annealing, the sample was quenched in air or in liquid nitrogen (LN_2). The change in oxygen content of the crystal after the annealing is small, as determined from the fact that the mass change of the sample after annealing is not detectable within the balance resolution of 0.05 mg.

The magnetic susceptibilities were measured in a magnetic field applied parallel to the c-axis of the crystal sample by using the Quantum Design SQUID magnetometer MPMS-XL. To minimize the flux trapping caused by field inhomogeneity or temperature variation, the magnetization was always measured during warming cycle under fixed fields ranging from 1×10^{-4} to 1 T and the sample was always positioned at the centre of the detecting coil during cooling or field adjustment. All the magnetic data were corrected for the demagnetization factor.[20]

3. Results and discussion

Shown in Fig.1 are the Meissner (field-cooled) and the shielding (zero-field-cooled) signals of the sample after thermal treatments, which were measured in a field of 5×10^{-4} T on warming.

Given in Fig.2 is the superconducting critical temperature (T_C) versus oxygen content for different annealing conditions, showing T_C increasing from 15.3 to 19 K. The onset T_C is derived from the magnetic measurements shown in Fig.1, and it is defined as the temperature at which the diamagnetic transition just starts. The various annealing conditions are indicated by letters from a to f, and described in the caption of Fig.2. It is clear that, in the underdoping regime, the rising tendency of T_C in Fig.2 is due to an increase in hole density by oxygen doping, since strontium doping is fixed at $x \sim 0.063$ for this crystal sample. Usually, the oxygen content of LSCO decreases when the crystal is heated at a higher temperature and a lower oxygen pressure, while it increases when annealed at a lower temperature and a higher oxygen pressure.

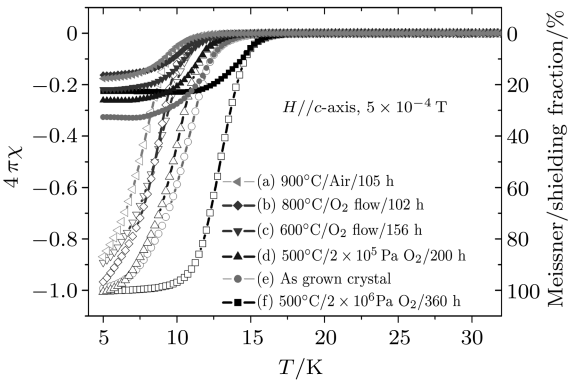


Fig.1. Meissner curves (solid symbol lines) and the shielding curves (open symbol lines) of $La_{1.937}Sr_{0.063}CuO_{4+\varepsilon}$ crystal thermally treated under various temperatures and oxygen pressures.

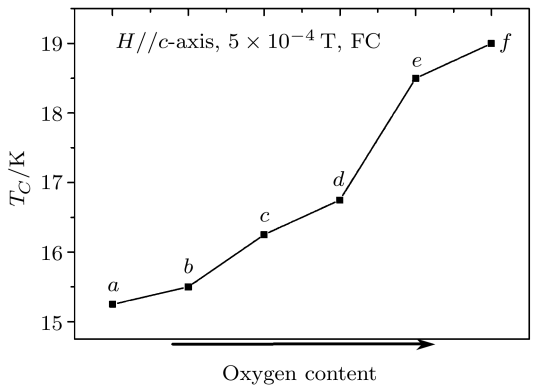


Fig.2. The change of superconducting transition temperature T_C by the thermal treatment for increasing oxygen content in $La_{1.937}Sr_{0.063}CuO_{4+\varepsilon}$ crystal: (a) 900°C in air/105 hours/quenched in LN_2; (b) 800°C in O_2 flow/102 hours/quenched in LN_2; (c) 600°C in O_2 flow/156 hours/quenched in air; (d) 500°C in 2×10^5 Pa O_2/200 hours/quenched in LN_2; (e) As-grown crystal; (f) 500°C in 2×10^6 Pa O_2/360 hours/quenched in air.

Plotted in Fig.3 is the temperature dependence of the differential of susceptibility with respect to temperature, $d\chi/dT$, under a field of 5×10^{-4} T for all the thermal treatments, in which the effect of increasing oxygen content on the electronic state can be clearly seen. For clarity, each curve is separated from each other by arbitrarily shifting vertically. We find that

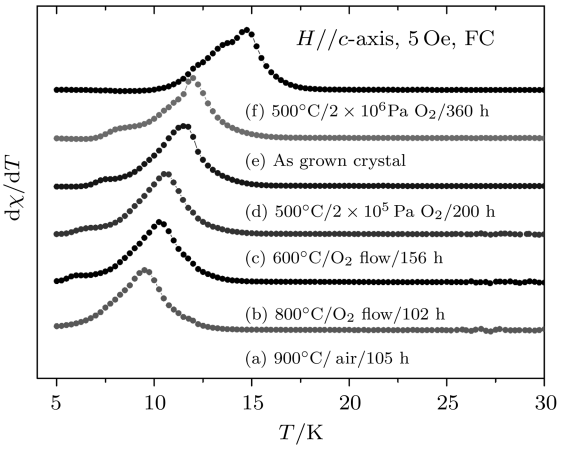


Fig.3. The temperature dependence of $d\chi/dT$ of $La_{1.937}Sr_{0.063}CuO_{4+\varepsilon}$ crystal annealed under various conditions.

the $d\chi/dT$ curve of the crystal with lower T_C only shows a single peak, indicating that there exists only a single superconducting phase, which is consistent with our previous results.[14,18] When T_C increases (i.e. at higher oxygen dopings), this single peak develops into a shape with a fine structure (see sample f heated at 500°C and 2×10^6 Pa O_2). This phenomenon indicates that an increase of interstitial oxygen content does not simply increase T_C, but also introduces a new subtle electronic state in addition to the primary electronic phase in the LSCO system. In order to further check this point, we have carried out a series of susceptibility measurements under various fields up to 1 T for the sample annealed at various temperatures. Figure 4 illustrates the corresponding differential curves of $d\chi/dT$ for the sample with the lower oxygen doping and T_C, showing a single transition peak. With increasing magnetic field, the single peak is broadened at higher fields, but the critical temperature T_C remains almost unchanged. This is a characteristic of an intrinsic superconducting phase. It has been reported[14] that the intrinsic superconducting phase is in a thermodynamically metastable state, and the increase of field only broadens its superconducting transition but its onset T_C is relatively robust under fields up to 5 T. In the case of the sample with higher oxygen content and T_C, however, the curves of $d\chi/dT$ exhibit a complicated structure (see Fig.5), as mentioned above. When the field increases, the structured peak gradually changes into a single peak at fields above 5×10^{-2} T. When the magnetic field continues to increase, the superconducting transition begins to broaden, with no significant change in T_C. This is again a characteristic of an intrinsic superconducting state.

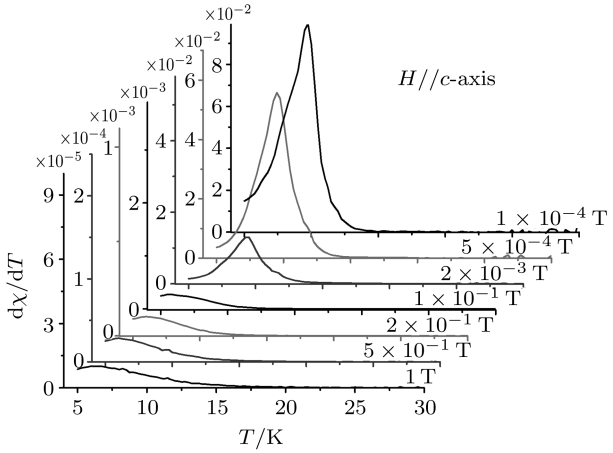


Fig.4. The temperature dependence of $d\chi/dT$ under various magnetic fields for the sample annealed in air at 900°C for 105 hours, showing a $T_C\sim15.3$ K.

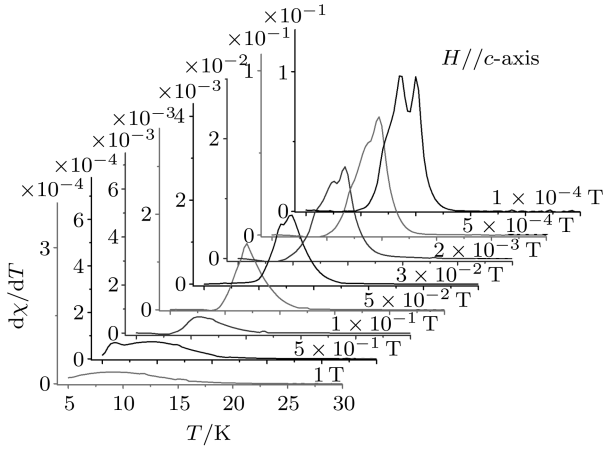


Fig.5. The temperature dependence of $d\chi/dT$ under various magnetic fields for the sample annealed at 500°C and 2×10^6 Pa O_2 pressure for 360 hours, showing a T_C of $\sim$ 19 K.

Now we can discuss the origin of the fine structure of the peak that appears in the differential curves for the sample with a higher oxygen doping. As shown in Fig.5, the fine structure of the peak can be easily suppressed by a magnetic field above 5×10^{-2} T. The

energy corresponding to such a low field is very small, and this field has no effect on the crystal structure. Therefore, we believe the fine structure of the peak does not result from the modification of crystal structure of the LSCO system, it is only of a pure electronic origin. The potential energy of a single spin in a magnetic field can be estimated from the Bohr magneton ($\mu_B = e\hbar/2\,m$). For example, for a field of 1 T, the potential energy is as small as ~ 0.06 meV. Hence, the easy suppression of this peak structure by a field above 5×10^{-2} T indicates that the corresponding electronic state induced by interstitial oxygen is very unstable, or, is not an intrinsic one. The new subtle electronic state occurring at higher oxygen doping may be related to electronic phase separation and charge inhomogeneity in the LSCO system. This phenomenon can be understood based on recently proposed composite charge model:[21] only a small fraction of the total doped holes contributes to the free charge transport and superconductivity, while the rest of the holes are in an ordered bound state, forming a 2D electronic (charge) lattice in the CuO_2 plane. In other words, charge doping not only adjusts free-carrier and superfluid densities, but may also affect or modulate the underlying competing charge ordering and electron inhomogeneity. In the present case of LSCO crystal with strontium doping level near a magic doping ($x \sim 0.063$), the electron system is predominated by the intrinsic state, and the subtle new electronic state introduced by moderate oxygen doping is so fragile that it can be easily suppressed by an applied magnetic field. At higher fields all the measurements of the sample exhibit a similar behaviour that an intrinsic superconducting phase would have. Our results indicate that, when the hole density is moderately changed by oxygen doping up to near the magic doping level, the underdoped LSCO system can still keep the feature of the intrinsic electronic state to some extent. However, it is worthwhile to point out that, if the charge density is greatly deviated from the magic doping level by introducing interstitial oxygen, the electron system of the underdoped LSCO will behave very differently:[22] there will emerge two coexisting intrinsic superconducting states with different T_C, as characterized by their robustness under an applied magnetic field. This can be attributed to the formation of multiple intrinsic electronic states stabilized by chemical phase separation due to a considerable introduction of interstitial oxygen.

4. Conclusions

In order to study the response of intrinsic electronic property to the moderate change in charge density of LSCO system by oxygen content near magic doping of $x = 1/16$ ($= 0.0625$), we have annealed the as-grown superconducting $La_{1.937}Sr_{0.063}CuO_4$ crystal under various temperatures and oxygen pressures to adjust the oxygen content in the crystal. With increasing oxygen doping, the critical temperature T_C of the annealed sample rises from 15.3 to 19 K. Systematic magnetic measurements have also been performed on the annealed crystal to trace the evolution of electronic states in the superconducting phase due to the moderate change in oxygen doping. It is found from the differential curves of $d\chi/dT$ that the annealed samples with a lower oxygen doping and T_C, only show a single intrinsic superconducting transition. However, in the sample with a higher oxygen content and T_C, there appears new subtle electronic state as indicated by the structured peak in $d\chi/dT$ curves. The new subtle electronic state is very fragile under a magnetic field. It can therefore be ascribed to a pure electronic phase separation and electronic inhomogeneity. This phenomenon can be understood based on the composite charge model[21] that free electrons and superfluid electrons innately coexist with underlying 2D charge ordering in CuO_2 plane. Our present experiments show that a moderate increase in oxygen doping does not significantly modify the intrinsic electronic state originally existing for oxygen content at the magic doping level, indicating that there is a tolerant region around the magic doping level for intrinsic electronic state. It is also pointed out that if the interstitial oxygen content is greatly increased so that chemical phase separation of doped oxygen becomes significant, there will emerge coexisting intrinsic superconducting states with different T_C in $La_{1.937}Sr_{0.063}CuO_{4+\delta}$,[22] a phenomenon very different from the present case.

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