

Microstructure and the superconductivity in $\text{La}_{2-x-y}\text{Sr}_x\text{Na}_y\text{CuO}_4$ systems

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The mechanism of high-temperature superconductivity is still an open question. Although the relationship between microstructure and superconductivity has been noticed in the early days, there is still lack of a definite explanation. In this paper we study the microstructure and the superconductivity of $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples and $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples. It is surprising that the doping of Na^+ does not introduce itinerant hole carriers into the CuO_2 plane. All $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples show insulatorlike behavior just like La_2CuO_4 . For $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples, they exhibit superconductivity even at Na doping content $y=0.30$. We suggest that the microstructure directly dominates the carrier concentration in the CuO_2 plane, so that it directly determines the occurrence of the superconductivity.

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I. INTRODUCTION

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is the only copper-oxide superconductor for which the chemical composition can be varied over a wide enough range to obtain the full spectrum of electronic properties. The undoped compound La_2CuO_4 is an insulating antiferromagnet in which the spin moments on adjacent Cu^{2+} ions are antiparallel. The bulk susceptibility of La_2CuO_4 shows the Néel like transition at 240 K, which indicates the long-range antiferromagnetic (AF) order.¹ It is commonly accepted that upon doping of bivalent ions at La site the charge neutrality requires that the electrons are removed from the CuO_2 planes, thereby effectively creating mobile holes in the planes. With increasing hole concentration, the compound evolves from an AF insulator to a superconductor.² The influence of Sr^{2+} doping on the carrier concentration of CuO_2 plane and on the conduction behavior of this system is of particular interest. It is crucial to clarify whether such behavior is intrinsic for these compounds or whether some simpler explanation, such as the effects of increasing carrier concentrations, a structural phase transition, or chemical phase separation, can explain the appearance of superconductivity.³

It is well known that upon doping La^{3+} by divalent ions (such as Sr^{2+} and Ba^{2+}) in La_2CuO_4 matrix, the charge carriers are introduced into the “parent” material. Electronic motion in these materials occurs primarily in the CuO_2 layers. In the cuprates the doped holes are believed to occupy oxygen $2p_\sigma$ orbitals which hybridize with the Cu $3d_{x^2-y^2}$ orbital to form a $d^9\bar{L}$ (\bar{L} ligand hole) configuration.^{4,5} It is possible to vary the electron density in the square lattice by doping such a compound to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, and then x measures the density of holes relative to the insulating state with one electron per site.^{6,7} Compared with the substitution of La^{3+} by the $2+$ ions, the substitution by monovalent ions, such as H^+ , Li^+ , Na^+ , K^+ , or Rb^+ , should be more effective to provide holes which are crucial to the superconductivity. Besides the difference of valence, another difference between Na^+ and Sr^{2+} lies on the ion radius. It is rather interesting to investigate the different behaviors of Na^+ dop-

ing and Sr^{2+} doping in La_2CuO_4 system. In this paper we present the experiments on the microstructure, the superconductivity, and the transport properties of $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples and $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples. We suggest that in La_2CuO_4 -based superconductors, the compressive stress in the CuO_2 plane is essential to the hybridization of the Cu $3d_{x^2-y^2}$ orbitals and the O $2p_\sigma$ orbitals, and this hybridization is essential to the introduction of hole carriers in the CuO_2 plane. Thus the compressive stress in La_2CuO_4 -based superconductors is necessary for the superconductivity. This result gives a definite explanation on the microstructure and the superconductivity.

II. EXPERIMENT

Polycrystalline samples of $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ ($y=0.02, 0.05, 0.1, 0.15, 0.3, 0.5$) and $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ ($y=0.02, 0.05, 0.1, 0.15, 0.3$) were synthesized by means of a conventional solid-state reaction method using high-purity powders of La_2O_3 , Na_2O_2 , SrCO_3 , and CuO . The mixed powders, pressed into pellets, were then reacted at $1100\text{--}1150^\circ\text{C}$ for 48 h under oxygen atmosphere. X-ray dif-

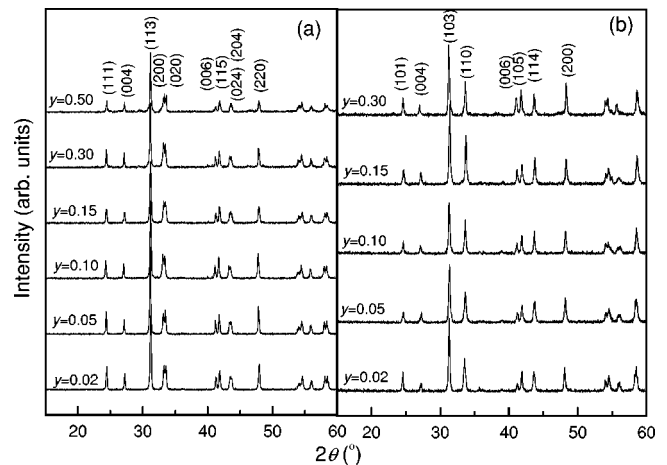


FIG. 1. The x-ray-diffraction patterns for (a) $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples and (b) $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples.

TABLE I. The unit-cell parameters of $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples.

$\text{La}_{2-y}\text{Na}_y\text{CuO}_4$	a (Å)	b (Å)	c (Å)	Cu-O (apical) (Å)	Cu-O (plane) (Å)	Cu-O-Cu bond angle (°)
0.02	5.3571	5.3969	13.1346	2.4042	1.9034	173.116
0.05	5.3517	5.3989	13.1372	2.4047	1.9039	173.117
0.10	5.3544	5.3982	13.1419	2.4055	1.9043	173.116
0.15	5.3583	5.3960	13.1473	2.4055	1.9046	173.114
0.30	5.3522	5.3947	13.1423	2.4056	1.9033	173.112
0.50	5.3548	5.3968	13.1397	2.4052	1.9037	173.113

fraction (XRD) analysis was carried out by a Rigaku-D/max- γ A diffractometer using high-intensity $\text{Cu-K}\alpha$ radiation to screen for the presence of an impurity phase and the changes in structure. The lattice parameters were determined from the d value of XRD peaks by a standard least-squares refinement method. X-ray-photoelectron spectroscopy (XPS) measurements were performed using ESCALAB MK II spectrometer with $\text{Mg-K}\alpha$ x-ray source and a resolution of 0.9 eV. The measurements of infrared (IR) transmission spectra (Nicolet 700) were carried out at room temperature with powder samples in which KBr is used as a carrier. Resistivity was measured using a standard four-probe method in a closed-cycle helium cryostat between 16 K and room temperature. The Hall-effect measurements were performed by a dc method in fields of up to 4 T using a six-probe geometry. The thermoelectric power $S(T)$ was measured by a differential method. The temperature of the samples was controlled automatically within the precision of 0.01 K, and the temperature gradient between both ends of the sample was 2 K. Magnetic susceptibility was measured by superconducting quantum interference device susceptometer (Quantum Design MPMS) under field cooled condition with 2 Oe.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray-diffraction patterns of $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples and $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples. XRD analyses indicate that $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples are crystallized in single-phase orthorhombic symmetry structure at room temperature and $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ are crystallized in single-phase tetragonal symmetry structure. The index of diffraction peaks has been marked according to the JCPDS-International Center for Diffraction Data 1990, 40-1100. The impurities, such as La_2O_3 , Na_2O , CuO , do not appear in the system. The x-ray-diffraction result convinces that the synthesized

samples are free from impurities and possess comparable quality as Na-free samples. The unit-cell parameters of $\text{La}_{2-x}\text{Na}_x\text{CuO}_4$ samples and $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples obtained by Rietveld analysis of the experimental XRD patterns are summarized in Tables I and II, respectively. Clearly the lattice parameters a , b , c , the apical O-Cu bond length, the in-plane O-Cu bond length, and the in-plane Cu-O-Cu bond angle of these two series of samples show little change with increasing Na doping content. While in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, previous studies have suggested that the c parameter expands slightly and the a and b parameters contract and finally lead to the stability of tetragonal structure above room temperature.^{3,8,9} We consider that this difference comes from the different ion radius of La^{3+} (1.17 Å), Sr^{2+} (1.32 Å), and Na^+ (1.16 Å). La_2CuO_4 has an intergrowth structure consisting of $(\text{LaO})_2$ rocksalt layers alternating with CuO_2 sheets. The tolerance factor of the structure is

$$t = \frac{\text{La-O}}{\sqrt{2}(\text{Cu-O})}. \quad (1)$$

In this case $t < 1$, the La-O bonds are in tension and the Cu-O bonds are in compression. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system, the substitution of La^{3+} by larger ions Sr^{2+} increases the tolerance factor and introduces compressive stress into Cu-O bonds. In $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ system, due to the similar ion ratio of La^{3+} (1.17 Å) and Na^+ (1.16 Å), the dopant of Na^+ does not introduce compressive stress into Cu-O sheet and does not straighten the Cu-O-Cu bond angle. Thus it remains orthorhombic structure at room temperature with increasing Na^+ doping content and remains an unchanged Cu-O bond length.

In order to testify that the Na^+ ions are introduced into the lattice, we carry out XPS measurements on these samples. As an example, in Fig. 1 we give the XPS results of $\text{La}_{1.7}\text{Sr}_{0.15}\text{Na}_{0.15}\text{CuO}_4$ sample. From Fig. 1 we notice that a peak located at 1071 eV which is corresponding to Na1s line. The atom proportions of all atoms concluded from the x-ray-

TABLE II. The unit-cell parameters of $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples.

$\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$	a (Å)	c (Å)	Cu-O (apical) (Å)	Cu-O (plane) (Å)	Cu-O-Cu bond angle (°)
0.02	3.7899	13.1807	2.4282	1.8949	180
0.05	3.7878	13.1995	2.4286	1.8939	180
0.10	3.7776	13.1811	2.4282	1.8888	180
0.15	3.7751	13.1901	2.4299	1.8876	180
0.30	3.7655	13.2025	2.4291	1.8828	180

TABLE III. The atom proportions of $\text{La}_{1.7}\text{Sr}_{0.15}\text{Na}_{0.15}\text{CuO}_4$ concluded from the X-ray-photoelectron spectroscopy. FWHM represents full width at half maximum.

Peak-ID	AT(%)	Center	FWHM	Area	Normal	S. F.	Stoic
Cu 2p3	14.32	933.95	4.30	2230	531	4.20	0.535
La 3d	26.74	834.95	6.85	9918	992	10.00	1.000
O 1s	21.78	528.25	1.60	533	807	0.66	0.815
O 1s	32.45	529.50	1.60	794	1203	0.66	1.214
Sr 3d	2.46	133.85	1.20	135	91	1.48	0.092
Na 1s	2.25	1071.07	1.00	192	83	2.30	0.084

photoelectron spectroscopy are listed in Table III. From Table III we find that the atom proportions are in accordance with the composition $\text{La}_{1.7}\text{Sr}_{0.15}\text{Na}_{0.15}\text{CuO}_4$. This result suggests that the Na^+ ions are introduced into the lattice.

In order to explore further the doping effects of Na^+ , the vibration modes of CuO_6 octahedron have been investigated by means of IR measurements because the vibration modes are effective to reflect the change of structure and other properties. Figures 2(a) and 2(b) show the infrared transmission spectra of $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples and $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples, respectively. For $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples, two infrared transmission peaks at $\nu_1 = 511.3 \text{ cm}^{-1}$ and $\nu_2 = 678.6 \text{ cm}^{-1}$ can be clearly observed within the frequency range of $350\text{--}800 \text{ cm}^{-1}$. With increasing Na^+ doping, ν_1 peak keeps steadily and ν_2 peak slightly shifts to high frequency. For $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples, only $\nu_1 = 503.7 \text{ cm}^{-1}$ peak can be observed within the frequency range of $350\text{--}800 \text{ cm}^{-1}$. We have carefully studied the infrared absorption spectra of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system.⁹ The ν_1 peak is assigned to the *c*-axis vibration mode and the ν_2 peak is assigned to the in-plane O-Cu stretching mode, and our previous report has suggested that the emergence of the ν_2 peak is always along with the metal-insulator transition in La_2CuO_4 -based compounds.⁹ The infrared absorption lines exhibit little change with increasing Na^+ doping, which indicates that the doping of Na^+ has little effect on the structure and vibration state in these systems.

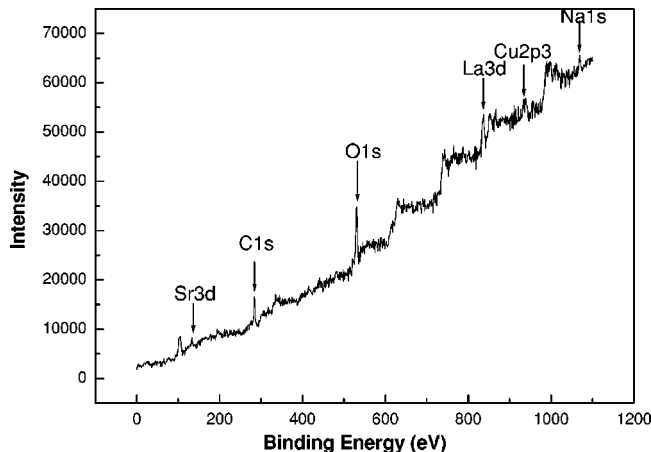


FIG. 2. The x-ray-photoelectron spectroscopy for $\text{La}_{1.7}\text{Sr}_{0.15}\text{Na}_{0.15}\text{CuO}_4$ sample.

Figures 3(a) and 3(b) show the temperature dependence of resistivity of $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples and $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples, respectively. It is obvious that all $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples exhibit semiconductorlike behavior and show no superconductivity at low temperatures. For $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples, it exhibits the superconductivity even at Na doping content $y = 0.30$. These results are quite surprising. According to the charge-transfer model, the substitution of monovalent Na^+ at the La^{3+} site would introduce twice as many hole carriers into the CuO_2 plane compared to the substitution of bivalent Sr^{2+} . Thus at a certain Na^+ doping content, the carrier concentration in $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ should be $2y$ per unit cell and the carrier concentration in $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ should be $0.15 + 2y$ per unit cell. Therefore, with increasing Na^+ doping, the $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ would exhibit the insulator-metal transition and superconductivity, and the superconductivity in the $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ would disappear as the system is driven to the overdoped regime.

In $\text{La}_{2-x-y}\text{Sr}_x\text{Na}_y\text{CuO}_4$ systems, Sr^{2+} is at the valence of +2 while Na^+ is at the valence of +1. According to the charge transfer model, doping of monovalent Na^+ ions in La_2CuO_4 would be easy to provide hole carriers into the CuO_2 plane comparing to doping of bivalent Sr^{2+} ions. However, our experimental results indicate the semiconductorlike conduction behavior of all $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples ($0 \leq x \leq 0.5$) and the superconductivity in all $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples ($0 \leq x \leq 0.3$). In Fig. 4(a) we

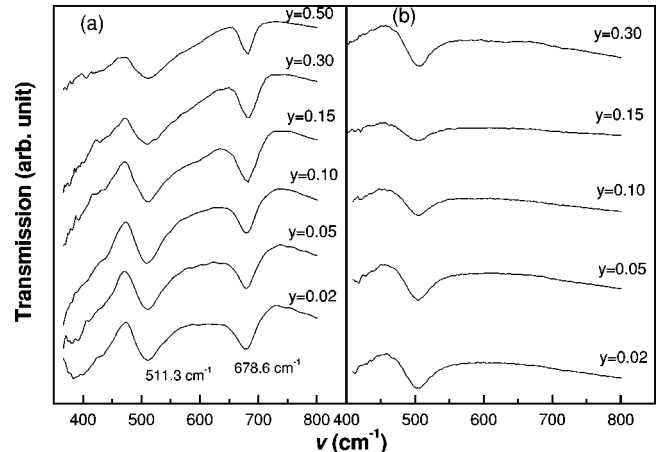


FIG. 3. Infrared transmission spectra for (a) $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples and (b) $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples.

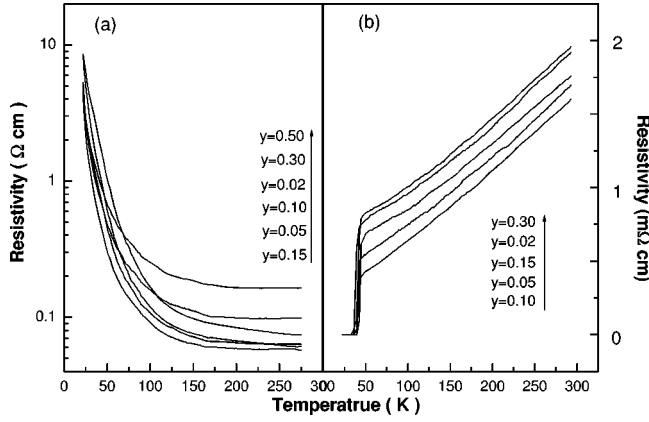


FIG. 4. The temperature dependence of resistivity for (a) $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples and (b) $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples.

show the temperature dependence of Hall coefficient for $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples. From Fig. 3(a) one can see that the carrier densities determined by Hall coefficient are very low in all $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples, and there is no obvious doping-dependent changes of either the magnitude or the shape of the Hall coefficient. The results of Hall coefficient indicate that the hole carriers are not introduced into the CuO_2 plane by the Na doping in $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ system. For the $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ system, we give the temperature dependence of thermoelectric power for these samples, as shown in Fig. 4(b). One can see that there is no obvious change of either the magnitude or the shape of the thermoelectric power. These results also imply that doping of Na^+ does not introduce itinerant hole carriers into the CuO_2 plane.

We also give the magnetic susceptibility for $\text{La}_{1.9}\text{Na}_{0.1}\text{CuO}_4$ sample as a function of temperature under field cooled condition with 2 Oe, as shown in Fig. 5(a). The bulk susceptibility on $\text{La}_{1.9}\text{Na}_{0.1}\text{CuO}_4$ shows the Néel-like transition at 240 K, which is quite similar to the result of undoped La_2CuO_4 . Thus we can conclude that the long-range AF order is not suppressed by Na doping in $\text{La}_{2-x}\text{Na}_x\text{CuO}_4$ system. It gives direct evidence that it does not introduce itinerant hole carriers into the CuO_2 plane by

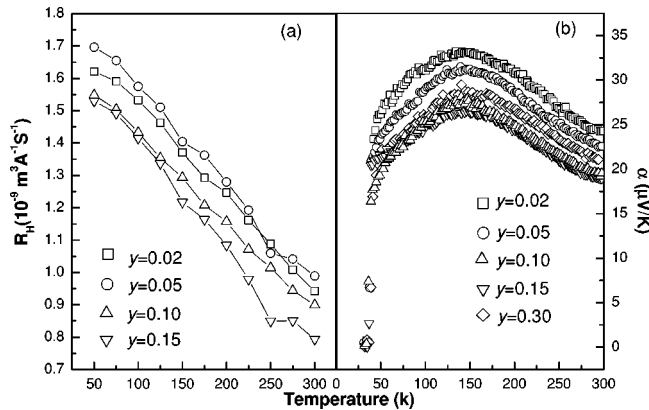


FIG. 5. (a) The temperature dependence of Hall coefficient for $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ samples and (b) the temperature dependence of thermoelectric power for $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples.

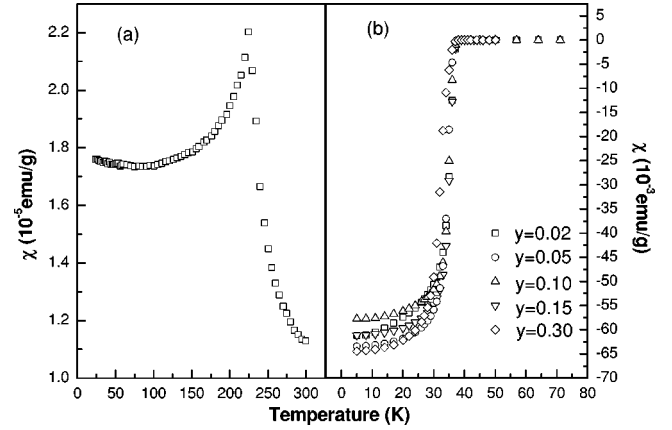


FIG. 6. The temperature dependence for magnetic susceptibility for (a) $\text{La}_{1.9}\text{Na}_{0.1}\text{CuO}_4$ sample and (b) $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples.

Na doping. Figure 5(b) shows the temperature dependence of magnetic susceptibility for $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples. From Fig. 5(b) one can see the T_c value keeps at 37 K for all samples, which is in accordance with the resistivity measurements.

In the parent compound La_2CuO_4 , there undergoes a cooperative tilting of the CuO_6 octahedron below an orthorhombic-tetragonal (OT) transition T_t due to the mismatch of the La-O and Cu-O equilibrium bond lengths, Fig. 6. Previous reports have revealed that the application of pressure on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ contributes to the OT transition and to the increase of T_c .^{7,10-12} In orthorhombic phase, T_c increases and the Cu-O-Cu bond straightens with pressure. In tetragonal phase, T_c is essentially pressure independent. In $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system the introduction of Sr^{2+} has equivalent effects on the OT transition and the superconductivity because the substitution of La^{3+} by larger ions Sr^{2+} would introduce compressive stress into the Cu-O bond and stabilize the tetragonal structure. This compressive stress on the Cu-O sheet leads to a shortened Cu-O bond length [from 1.904 Å ($x=0$) to 1.886 Å ($x=0.15$) at room temperature]. However, in $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ system, due to the similar ion radius of La^{3+} and Na^+ , it does not introduce compressive stress into the Cu-O bond and therefore does not undergo the OT transition with increasing Na doping content (the Cu-O bond length keeps constantly of 1.904 Å). It is obvious that the doping of Na has little influence on the transport properties in the $\text{La}_{2-y}\text{Na}_y\text{CuO}_4$ system. In $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples, doping of Na also has little influence on the structure (the Cu-O bond length keeps constant at 1.886 Å) and the transport property. It means that the occurrence of superconductivity in $\text{La}_{1.85-y}\text{Sr}_{0.15}\text{Na}_y\text{CuO}_4$ samples is due to the Sr^{2+} doping but not to the Na^+ doping. Thus we conclude that in both systems, the doping of Na^+ does not introduce hole carriers into the CuO_2 plane. We suggest that in La_2CuO_4 -based systems, the compressive stress is necessary for introduction of hole carriers into the CuO_2 plane. With the doping of monovalent or divalent ions, there are holes introduced into the O site. However, if there is no compressive stress, the holes are located at the O site. With the in-

introduction of compressive stress, the Cu-O bond length in the CuO₂ plane is shortened and the Cu $3d_{x^2-y^2}$ orbitals and the O $2p_\sigma$ orbitals overlap is strengthened at a certain degree (the so-called hybridization). Due to this hybridization, the holes become itinerant and is shared by the Cu $3d_{x^2-y^2}$ orbitals and the O $2p_\sigma$ orbitals. When there are itinerant hole carriers in the CuO₂ plane, the system shows an insulator-metal transition. And at a certain degree of hybridization, the superconductivity occurs. Departure from this degree, the superconductivity weakens. In La₂CuO₄ the copper is in the +2 valence state. The addition of Sr, Ba, and excess oxygen introduces the compressive stress which is in favor of the $pd\sigma$ hybridization and forces some of the Cu ions into the +3 valence state. The preservation of Cu³⁺ is essential to the superconductivity. However, in La_{2-y}Na_yCuO₄ the addition of Na does not introduce the compressive stress and the Cu ions remain at the +2 valence state. There may exist some oxygen vacancies. Thus the doping of Na does not contribute to the superconductivity.

We now consider why our results are important to the understanding of high- T_c superconductivity. They provide evidence that the compressive stress is essential to the introduction of hole carriers into the CuO₂ plane. The compressive stress induced by the doping of larger ion Sr²⁺ makes the Cu-O-Cu bond angle changes from 173.1° to 180° of La_{2-x}Sr_xCuO₄ and the itinerant charge carriers are introduced into the parent material. Although it is expected that Na⁺ doping should be more effective, compared to Sr²⁺ doping, to introduce hole carriers to the system, from Table I we notice that the doping of Na⁺ does not change the Cu-O-Cu bond angle even at a doping content of $y=0.3$. Thus it cannot provide hole carriers into the compound. These facts distinctly indicate that the superconductivity occurs at the Cu-O plane without distortion. With the decrease of Cu-O-Cu distortion, the overlap between the Cu $3d_{x^2+y^2}$ orbitals

and the O $2p_{xy}$ orbitals strengthens, thus leads to a strength of the $pd\sigma$ hybridization. When the $pd\sigma$ hybridization is at a certain degree, the electrons can easily be transferred from an O $2p_{xy}$ orbital to adjacent Cu $3d_{x^2+y^2}$ orbital and the system exhibits metallike behavior. When the CuO₂ plane is not disturbed, it favors the superconductivity. Therefore, the above results indicate that the occurrence of the superconductivity is not only related to the carrier concentration in the CuO₂ plane but also related to the degree of the hybridization between the Cu $3d_{x^2+y^2}$ orbitals and the O $2p_\sigma$ orbitals. Based on above discussion, we conclude that the dominance of microstructure on the superconductivity is intrinsic. The microstructure directly determines the carrier concentration in the CuO₂ plane.

IV. CONCLUSION

In summary, the microstructure, magnetic and transport properties of La_{2-y}Na_yCuO₄ samples and La_{1.85-y}Sr_{0.15}Na_yCuO₄ samples are studied. The experimental results indicate that doping of Na⁺ has little influence on the superconductivity and transport properties in the La₂CuO₄ and La_{1.85}Sr_{0.15}CuO₄ systems. The results could not be explained by using the charge-transfer model. We suggest that the introduction of compressive stress in La₂CuO₄ system is necessary for the superconductivity. Na⁺ ions have similar radius as La³⁺ ions. Thus it does not introduce compressive stress by Na⁺ doping and thus doping of Na⁺ has little influence on the microstructure and the superconductivity.

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