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Superconducting properties in $La_2CuO_{4+\delta}$ with excess oxygen

Toshikazu Hirayama, Masahito Nakagawa, Akihiko Sumiyama, and Yasukage Oda
Department of Material Science, Faculty of Science, Himeji Institute of Technology, 1475-2, Kanaji, Kamigori-cho,
Ako-gun, Hyogo, 678-1297, Japan

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We have studied the thermal history dependence of the superconducting properties below and above room temperature (RT) in the ceramic $La_2CuO_{4+\delta}$ with excess oxygen, which were prepared by annealing in high-pressure oxygen gas or electrochemical oxidation. The diffusion of the excess oxygen is concluded not to occur below RT. In the sample with small δ, the low T_c (32 or 36 K) superconducting phase appears, of which T_c is changed by the annealing at about 200 K. This change is presumably due to some phase transition without the diffusion of the excess oxygen. On the other hand, when δ reaches some threshold, another single superconducting phase with high T_c (45 K), which is stable below 373 K at least, appears. This sample was prepared by the electrochemical oxidation at 333 K for more than 48 h, where the excess oxygen can diffuse. In the sample electrochemically oxidized at RT, both the low- and high-T_c superconducting phases were formed only near the surface area of the sample. These phases were homogenized by annealing at 373 K.
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I. INTRODUCTION

As is well known, La_2CuO_4 (insulating and antiferromagnetic) becomes superconducting $La_2CuO_{4+\delta}$ by the intercalation of excess oxygen. The phase separation—the oxygen-rich phase (superconducting) and the oxygen-poor phase (antiferromagnetic)—is reported to occur at T_{ps} (phase separation temperature) in $La_2CuO_{4+\delta}$. The phase separation is accompanied with the diffusion of excess oxygen.[1] Moreover, the T_{ps} is dependent on the value of δ,[2–4] and the phase separation is suppressed in the samples with δ of 0.08 and 0.12.[5] In our previous papers, we have reported that the samples annealed in high-pressure oxygen gas have three superconducting phases with a T_c of 32, 36, and 45 K. The T_c of 32 or 36 K was changed by annealing at about 200 K. The amount of the phase with a T_c of 45 K was very small.[6] We have reported that the samples electrochemically oxidized at RT (room temperature) have a large amount of the 45 K phase, coexistent with the phase with a T_c of 32 or 36 K. The T_c of 45 K does not depend on the thermal history below RT,[7] also shown in another paper.[4]

First in this paper, we report the thermal history dependence of the superconducting properties below and above RT,[8] as for the samples that were prepared by annealing in high-pressure oxygen gas or the electrochemical oxidation at RT. Second, the superconducting properties of the samples electrochemically oxidized above RT, where the excess oxygen can diffuse, have been studied.

II. SAMPLE PREPARATION AND MEASUREMENT

The stoichiometric ceramic La_2CuO_4 was prepared by the solid-state reaction. Then it was annealed in oxygen gas at 100 and 650 bar. The bulk density of ceramic La_2CuO_4 was approximately 5.3 g/cm^3 and the size of each grain was approximately 5∼7 μm. The values of δ in these samples were 0.012 and 0.022, respectively, measured by the weight gain measurement. Here, of course, the value of δ is the averaged one in the whole sample. Also, we treated the sample with electrochemical oxidation at RT or at 333 K. The oxidation cell was set up as La_2CuO_4/1 N-KOH/Pt, where the working electrode was ceramic La_2CuO_4 and the counter electrode was Pt plate. The dimensions of ceramic La_2CuO_4 were $0.3\times3.0\times7.0$ mm^3 thin slabs for the measurements shown in Sec. III A, Sec. III B, and $1.5\times3.0\times7.0$ mm^3 slabs for the measurements shown in Sec. III C. The electrochemical potential was referred to the AgCl/Ag reference electrode. The oxidation was carried out by the following processes: at RT under an anodic potential of 450 mV (vs AgCl/Ag) for 24 h or at 333 K under an anodic potential of 600 mV (vs AgCl/Ag) for 24–72 h. The values of δ in the electrochemically oxidized samples were uncertain. In order to study the thermal history dependence above RT, the following processes were performed before the measurements: the samples were annealed at 373 K in air for 3 h, then quenched to 77 K in a few seconds or slowly cooled down to RT in 10 h.

The dc susceptibility $\chi_{dc}-T$ data were measured using a commercial superconducting quantum interference device magnetometer (MPMS2, Quantum Design, USA). In order to maintain a small residual magnetic field in the magnetometer, all measurements were performed below $H_a=20$ Oe after the initial cooldown from room temperature to liquid-He temperature. The residual magnetic field was about -1.5 mOe, measured by the high-purity (5 N) Pb sphere. The magnetic field induced by the offset current was estimated to be approximately -36 mOe. A magnetic field was applied parallel to the longer side of the samples, and the demagnetization factor corrections were not applied. In our measurements, the susceptibility changed monotonously below the T_c onset. At low enough temperature (∼4.5 K), the values of diamagnetism of the bulk samples were comparable with that of the powder samples in field cooling measurements. The resistivity $\rho-T$ data were obtained by the four-probe method. Also, the crystal structure analysis was performed by powder x-ray diffraction at RT.

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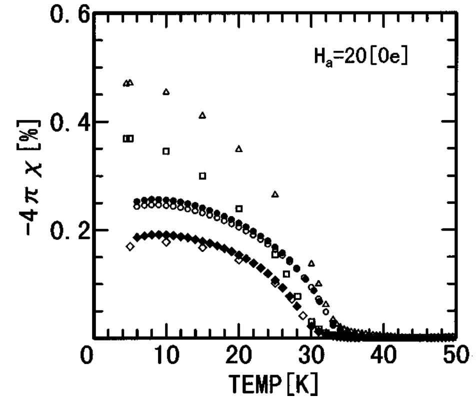

FIG. 1. Temperature dependence of susceptibility (FC:field cooling) of $La_2CuO_{4.012}$. The vertical axis shows a percentage of the perfect diamagnetism. In the following cases, the annealing at 220 K increased T_c by about 4 K. (1) After quenching from RT to 77 K (open squares), then annealing at 220 K for 3 h (open triangles). (2) After annealing at 373 K for 3 h and quenching to 77 K (open diamonds), then annealing at 220 K for 3 h (open circles). (3) After annealing at 373 K for 3 h, slowly cooling to RT and quenching to 77 K (solid diamonds), then annealing at 220 K for 3 h (solid circles).

III. RESULTS AND DISCUSSIONS

A. Thermal history dependence of the superconducting properties below and above RT

The susceptibility $\chi_{dc}-T$ data of the bulk sample annealed in oxygen gas at 100 bar; δ=0.012, are shown in Fig. 1. The low-T_c onset of 32 or 36 K is dependent on thermal history around 200 K; this result is consistent with the measurements from Oda and Yamada,[6] Ryder *et al.*,[9] and Ahrens *et al.*[10]

However, in the present study, the T_c onset of 32 K has been found not to be changed in the following three cases, as shown in Fig. 1: (1) the measurement after quenching from RT down to 77 K, (2) the measurement after quenching from 373 down to 77 K, and (3) the measurement after slowly cooling from 373 K down to RT and quenching from RT down to 77 K. These results imply that the distribution of the excess oxygen is not changed between RT and 373 K. The phase separation with the oxygen-rich and the oxygen-poor phase might be achieved above 373 K in this sample. The T_c onset of 32 K was changed into 36 K by the annealing at 220 K. However, the change of T_c onset from 32 to 36 K was not obtained by the annealing below 180 K, reported previously.[7] This result means that the long-range diffusion of the excess oxygen does not exist below 180 K, at least.

Thus, the superconducting transition temperature of the phase that is stable over the temperature range from RT to 373 K, at least, is concluded to be 32 K (onset) in this sample. And the T_c of the phase that is stable below about 200 K is 36 K. The decrease of magnitude of diamagnetism after the annealing at 373 K may be induced by the decrease of excess oxygen during the annealing at 373 K.

Shown in Fig. 2 is the susceptibility data of the samples with δ of 0.012 and 0.022, prepared by the annealing in high-pressure oxygen gas. The T_c onset, obtained after the quenching from RT to 77 K, was 32 K in both samples with δ of 0.012 and 0.022, which was the averaged value in the whole sample. The result in the sample with δ of 0.012 reconfirms the result given in Fig. 1. This implies that the T_c onset was independent of the ''averaged'' δ in these samples, suggesting that the stoichiometry of the superconducting phases are independent of the δ, although the volume fraction must be changed with the δ. The T_c onset of 32 K became 36 K in the case of slowly cooling from RT to 77 K, as well as in the case of annealing around 200 K in Fig. 1.

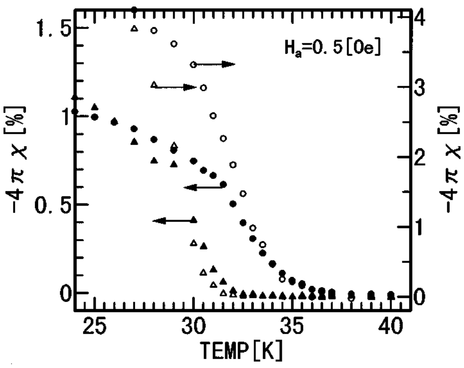

FIG. 2. Temperature dependence of susceptibility (FC) of $La_2CuO_{4+\delta}$ annealed in high-pressure oxygen gas. The vertical axis shows a percentage of the perfect diamagnetism. The data were obtained after quenching (solid triangles: δ=0.012/open triangles: δ=0.022) and after slow cooling (solid circles: δ=0.012/open circles: δ=0.022) from RT down to 77 K.

These results imply that the coexistence (phase separation) of the oxygen-rich and the oxygen-poor phase is already achieved above RT in both samples with δ of 0.012 and 0.022, while our results might be inconsistent with the reported $\delta-T$ phase diagram.[2–4] It is concluded that the T_c onset of the superconducting phase that is stable above about 200 K is 32 K in the samples with δ of 0.012 and 0.022. And the one that is stable below 200 K is 36 K.

Figure 3 shows the $\chi_{dc}-T$ data of the sample electro-

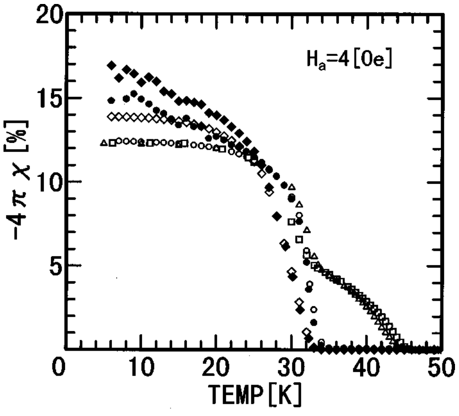

FIG. 3. Temperature dependence of susceptibility (FC) of $La_2CuO_{4+\delta}$ electrochemically oxidized at RT for 24 h. The vertical axis shows a percentage of the perfect diamagnetism. The symbols show the following cases: (1) after quenching from RT to 77 K (open squares), then annealing at 220 K for 3 h (open triangles), (2) after annealing at 373 K for 3 h and quenching to 77 K (open diamonds), then annealing at 220 K for 3 h (open circles): and (3) after annealing at 373 K for 3 h, slowly cooling to RT and quenching to 77 K (solid diamonds), then annealing at 220 K for 3 h (solid circles).

chemically oxidized at RT for 24 h. In comparison with the $\chi_{dc}-T$ data from Chou, Cho, and Johnston,[11] the value of δ of this sample might be estimated to be between 0.07 and 0.10. Just after the oxidation, the coexistence of two different superconducting phases (T_c onsets of 32 and 45 K) was clearly observed (open squares and open triangles), as reported in some papers.[7,11,12] The low T_c of 32 K was increased by annealing around 200 K, suggesting the transition into the 36 K phase, as in the cases of Figs. 1 and 2. However, the high-T_c (45 K) phase was independent of the thermal history around 200 K. It should be noted that the high-T_c (45 K) phase disappeared after annealing at 373 K, which was also confirmed by resistivity measurements not shown in this paper. Similar phenomena were observed in some papers,[13,14] although the details were not well explained. The Meissner signals, measured immediately after electrochemical oxidation at RT, were not changed in more than 2 months and are not shown in this paper. This implies that the distribution of the excess oxygen is not changed at RT for a long time, suggesting that no diffusion of the excess oxygen exists at RT. However, after the annealing at 373 K, the high-T_c (45 K) phase apparently changed to the low-T_c (32 or 36 K) phase, which was caused by the change of distribution of the excess oxygen, accompanied with the diffusion of the excess oxygen. The low-T_c phase was formed at 373 K.

From these results in Figs. 1, 2, and 3, the long-range diffusion of the excess oxygen has been concluded not to occur below RT, but to occur at 373 K. The change of T_c onset between 32 and 36 K, which depends on the thermal history around 200 K, may be due to some phase transition or some structural change without the long-range diffusion of excess oxygen. This suggestion may be consistent with the reports from Kyomen *et al.*[15] and Xiong *et al.*[16] Preliminary discussions have been reported in our previous paper.[8]

B. Superconducting properties in the sample electrochemically oxidized above RT

In order to obtain higher oxidation levels, the electrochemical oxidation, accompanied by the diffusion of the excess oxygen, was expected to be useful. For this purpose, the electrochemical oxidation was carried out at 333 K for more than 24 h. The electrochemical oxidation at 373 K was not adopted because of much evaporation of the 1 N-KOH solution. This resulted in the gradual change of superconducting behaviors as the oxidation time increased: (1) the single low-T_c (32 or 36 K) phase (oxidation time=24 h), (2) the coexistence with the low and the high-T_c (45 K) phase (36 h), and (3) the single high-T_c phase (48 and 72 h), as shown in Figs. 4 and 5; $\chi_{dc}-T$ data. These behaviors were also confirmed in the resistivity data, not shown in this paper. At the same time, it also showed a gradual enhancement of the Meissner volume fraction. In the samples oxidized for more than 48 h, the metallic behavior was observed in the normal resistivity data, as shown in Fig. 6, as observed in the single crystal fully oxidized at δ=0.13.[12] These results imply that the excess oxygen can diffuse even at 333 K, as we expected.

The single high-T_c (45 K) phase, obtained by oxidation at 333 K for more than 48 h, was *not* changed into the low-T_c (32 or 36 K) phase even by annealing at 373 K, in contrast with the result in the sample electrochemically oxidized at RT. This means that the high-T_c (45 K) phase becomes stable below 373 K, at least, when enough excess oxygen exists. Such samples can be achieved by electrochemical oxidation, which is accompanied by the diffusion of excess oxygen.

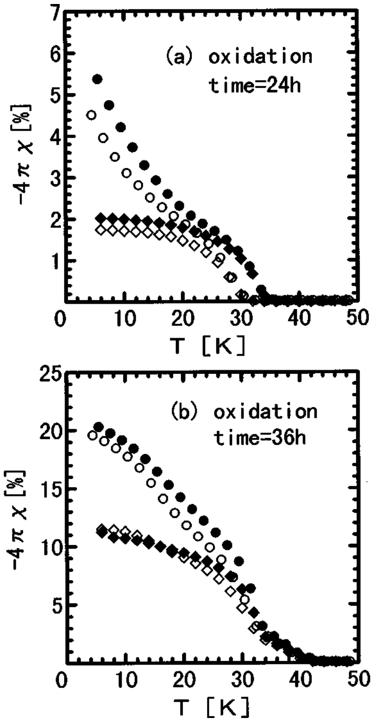

FIG. 4. Temperature dependence of susceptibility data of $La_2CuO_{4+\delta}$ electrochemically oxidized at 333 K (a) for 24 h and (b) for 36 h, in an applied magnetic field H_a=4 Oe. The vertical axis shows a percentage of the perfect diamagnetism. The symbols show the following cases: after quenching from RT to 77 K (open circles: ZFC (zero field cooling)/open diamonds: FC), then annealing at 220 K for 3 h (solid circles: ZFC/solid diamonds: FC).

As for the sample electrochemically oxidized at 333 K for 72 h, the x-ray-diffraction pattern showed a well-crystallized

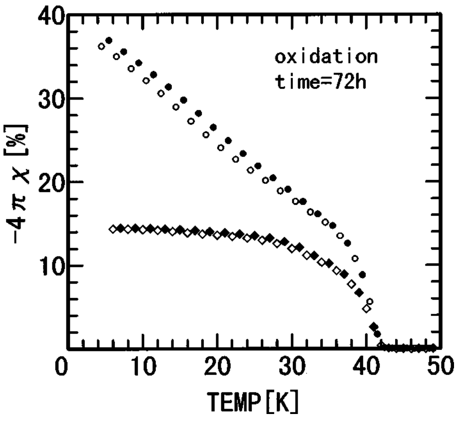

FIG. 5. Temperature dependence of susceptibility data of $La_2CuO_{4+\delta}$ electrochemically oxidized at 333 K for 72 h, in an applied magnetic field H_a=4 Oe. The vertical axis shows a percentage of the perfect diamagnetism. The symbols show the following cases: after quenching from RT to 77 K (open circles: ZFC/open diamonds: FC), then annealing at 220 K for 3 h (solid circles: ZFC/solid diamonds: FC).

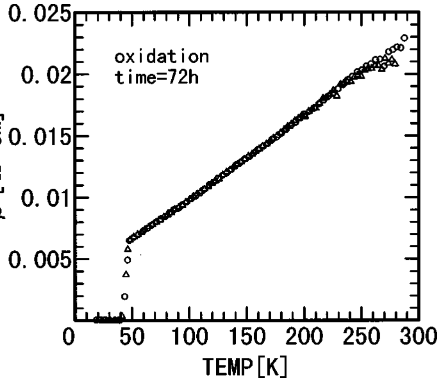

FIG. 6. Temperature dependence of resistivity data of $La_2CuO_{4+\delta}$ electrochemically oxidized at 333 K for 72 h. The metallic behavior is observed in the normal resistivity. The cooling processes (open circles) and the heating processes (open triangles).

character, but it exhibited enhanced orthorhombic distortion: a growth of the c axis and a growth of the difference between the a axis and the b axis, after electrochemical oxidation at 333 K for 72 h, as shown in Fig. 7 and Table I. These results were consistent with the neutron-diffraction data.[5]

C. Formation of the superconducting phases

The single high-T_c (45 K) phase was obtained by electrochemical oxidation at 333 K for more than 48 h, in contrast with the case of the sample electrochemically oxidized at RT. This may be explained in the following.

1. Surface oxidation in the sample electrochemically oxidized at RT

From the above results and discussions, in the sample electrochemically oxidized at RT, the diffusion of excess oxygen has been concluded not to occur below RT. So the insertion of excess oxygen into the inner part of the sample is supposed to be suppressed. Moreover, the high-T_c (45 K) phase undoubtedly has a higher density of excess oxygen than that of the low-T_c (32 K) phase, because the high-T_c phase appears only after long-time oxidation.

Therefore, we suppose that the high-T_c (45 K) phase is formed in the surface of the sample with a high density of excess oxygen, which may correspond to the suggestion by Chou *et al.*[12] As the density of the excess oxygen is discrete, the low-T_c (32 or 36 K) phase should exist inside the high-T_c phase near the surface. Little excess oxygen is inserted into the inner part of the sample, where the antiferromagnetic phase still exists. This image is presented in Fig. 8(a). When this sample is annealed at 373 K, the excess oxygen can diffuse into the inner part. Finally the excess oxygen is distributed in the whole sample, and forms the low-T_c phase with a low density of the excess oxygen.

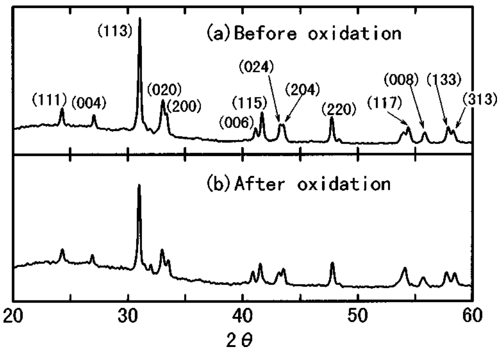

FIG. 7. The x-ray-diffraction pattern of $La_2CuO_{4+\delta}$ (a) before, $\delta=0$, and (b) after, $\delta\neq0$, electrochemical oxidation at 333 K for 72 h.

TABLE I. The lattice constant and the volume in the $La_2CuO_{4+\delta}$ unit cell before and after electrochemical oxidation at 333 K for 72 h.

	a (Å)	b(Å)	c (Å)	Volume (Å^3)
La_2CuO_4	5.3632	5.4162	13.179	382.84
$La_2CuO_{4+\delta}$	5.3446	5.4334	13.252	384.84

This scenario explains the behaviors in the sample electrochemically oxidized at RT; the coexistence of the high- (45 K) and the low (32 or 36 K) T_c onset was achieved just after oxidation at RT, and the high-T_c phase is changed into the low-T_c phase by annealing at 373 K.

2. Full oxidation in the sample electrochemically oxidized at 333 K

On the other hand, in the sample electrochemically oxidized at 333 K, the diffusion of the excess oxygen is accelerated, so that the excess oxygen can be distributed in the whole sample in a short time (⩽24 h) during the oxidation. The low-T_c (32 or 36 K) phase is formed first in the whole sample. More oxidation makes the high-T_c (45 K) phase with a high density of the excess oxygen, coexistent with the low-T_c phase. The oxidation at 333 K, for more than 48 h, makes the nearly single high-T_c (45 K) phase, as shown in Fig. 8(b). A small amount of the low-T_c phase may still exist after the electrochemical oxidation at 333 K for more than 48 h, because a slight change in Fig. 5 was observed after the annealing at 220 K.

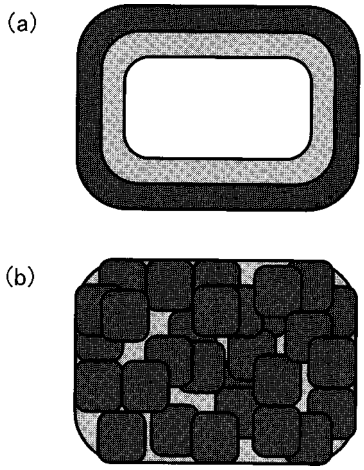

FIG. 8. The formation of the superconducting phase in $La_2CuO_{4+\delta}$ electrochemically oxidized at (a) RT and (b) 333 K. The darkly shaded area indicates the high T_c (45 K) phase and the lightly shaded one indicates the low T_c (32 or 36 K) phase. In each phase, the density of the excess oxygen should be homogeneous. The white area is the antiferromagnetic phase (oxygen-poor phase).

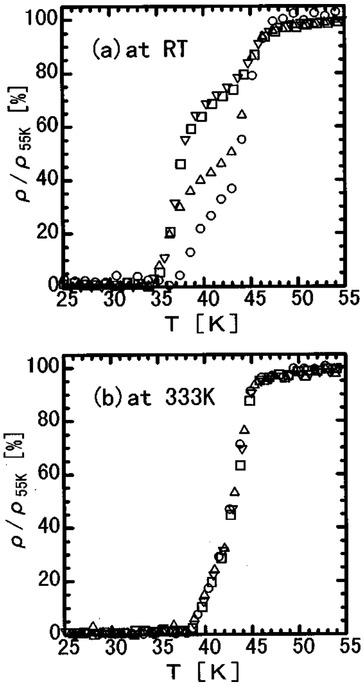

FIG. 9. The resistivity $\rho - T$ data of $La_2CuO_{4+\delta}$ electrochemically oxidized at (a) RT for 24 h and (b) 333 K for 72 h. The data are normalized by the resistivity data at 55 K to emphasize the superconducting transition: immediately after oxidation (open circles) and after removing all the surfaces up to 150 μm (open triangles), 250 μm (open squares), 500 μm (open inverted triangles) deep.

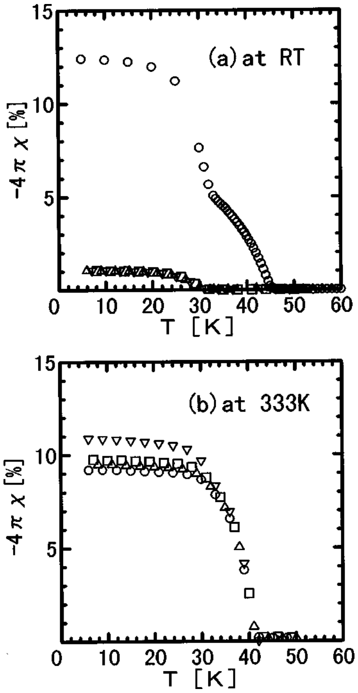

FIG. 10. The susceptibility $\chi_{dc} - T$ data (FC) of $La_2CuO_{4+\delta}$ electrochemically oxidized at (a) RT for 24 h and (b) 333 K for 72 h, in a magnetic field $H_a = 4$ Oe: immediately after oxidation (open circles) and after removing all the surfaces up to 150 μm (open triangles), 250 μm (open squares), 500 μm (open inverted triangles) deep. The vertical axis shows a percentage of the perfect diamagnetism.

We have concluded that the phase with a T_c onset of 45 K is the stable phase below 373 K, when the sample is saturated with the high-T_c phase. This conclusion may be in contrast with the suggestion that the 45 K phase is the metastable phase.[13,14]

In order to confirm these explanations, we checked the changes of the superconducting properties after removing all the surfaces of the samples electrochemically oxidized at RT or at 333 K by polishing with emery papers. The resistivity and susceptibility data are shown in Figs. 9 and 10, respectively.

In the sample electrochemically oxidized at RT, the high-T_c (45 K) phase decreased drastically after removing the surfaces up to more than 150 μm deep, which implies that the high-T_c (45 K) phase was formed in the surface area of this sample. However, in the sample electrochemically oxidized at 333 K, the superconducting properties were little changed by removing the surfaces of the sample. The excess oxygen is diffused by the electrochemical oxidation at 333 K, and is distributed in the whole sample. So, the high-T_c phase is formed in the whole sample. These conclusions support the explanations, described above, strongly.

IV. CONCLUSION

The long range diffusion of the excess oxygen has been concluded not to occur below RT and to exist above 333 K. When δ is small, the low-T_c (32 or 36 K) superconducting onset appears. The low T_c is changed from 32 to 36 K by annealing at about 200 K, which is probably due to some phase transition without the long-range diffusion of the excess oxygen. Also, the phase separation (the oxygen-rich low T_c phase and the oxygen-poor phase), accompanied with the diffusion of the excess oxygen, may occur above 373 K in the sample with δ of 0.012.

On the other hand, when δ reaches some threshold, we have obtained another single superconducting phase with high T_c (45 K). This phase has been obtained by the electrochemical oxidation at 333 K for more than 48 h. This showed a metallic behavior in the normal resistivity, and was concluded to be the stable phase below 373 K, at least. Also this high-T_c phase was distributed in the whole sample after electrochemical oxidation at 333 K for more than 48 h.

The superconducting transition temperature of 45 K is higher than the maximum T_c of 37 K obtained by hole doping with Ba or Sr. It is interesting to study the origin of the T_c enhancement. The structural distortion due to the intercalation of the excess oxygen may play an important role for this enhancement.

In the sample electrochemically oxidized at RT for 24 h, both the low- (32 or 36 K) and the high- (45 K) T_c phase are formed near the surface area of the sample. These phases can be homogenized in the whole sample, and the high-T_c phase changes into the low-T_c phase after annealing at 373 K.

ACKNOWLEDGMENTS

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